



Nuclear spin-lattice relaxation time measurement in $\text{NaD}_3(\text{SeO}_3)_2$
by Roy Reinhart Knispel

A thesis submitted to the Graduate Faculty in partial fulfillment of the requirements for the degree of
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Abstract:

Nuclear magnetic resonance and electrical conductivity-measurements were used to study the motions of hydrogen nuclei in deuterated sodium trihydrogen selenite crystals.

From electrical conductivity measurements, deuteron spin-lattice relaxation time measurements and direct deuteron interbond jump time measurements, an activation energy of 0.73 ± 0.07 eV for deuteron interbond jumping was obtained. This motion provides the dominant contribution to the spin-lattice relaxation time above 40°C . In the temperature region from about 10°C to the ferroelectric transition temperature (-25°C to -35°C in the crystals studied) a high frequency motion, such as deuteron intrabond motion, was found to dominate the spin-lattice relaxation process.

The activation energy for this motion was found to be 0.055 ± 0.01 eV. Below the ferroelectric transition, the deuteron spin-lattice relaxation time was found to be too short to be due to spin diffusion to paramagnetic impurities. This implied the presence of some molecular motion in which the deuterons are involved below the transition temperature, and a possible explanation was found in considering the contribution of torsional oscillations of SeO_3 groups to the spin-lattice relaxation time of the deuterons. The temperature and frequency dependence of the spin-lattice relaxation time of Na^{23} nuclei were similar to those of the deuterons over the same temperature and frequency ranges. The possibility of deuteron motion contributing to Na^{23} relaxation was therefore considered. In the 30°C to 80°C range, where deuteron interbond jumping is the dominant deuteron relaxation mechanism, it was found that the Na^{23} relaxation showed too small an activation energy (0.35 eV) to arise from deuteron interbond jumping. The indication of deuteron intrabond motion in the paraelectric phase is indicative of a dynamic order-disorder type ferroelectric phase transition. Evidence that the transition is not exclusively of this type, however, was found in the fact that the suppression of intrabond motion with the onset of polarization cannot explain the decrease in the deuteron spin-lattice relaxation time observed in the temperature region below the transition.

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IN $\text{NaD}_3(\text{SeO}_3)_2$

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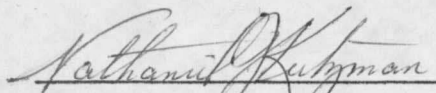
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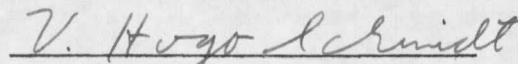
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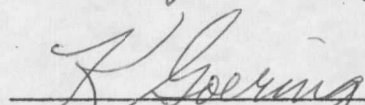
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ABSTRACT

Nuclear magnetic resonance and electrical conductivity measurements were used to study the motions of hydrogen nuclei in deuterated sodium trihydrogen selenite crystals. From electrical conductivity measurements, deuteron spin-lattice relaxation time measurements and direct deuteron interbond jump time measurements, an activation energy of 0.73 ± 0.07 eV for deuteron interbond jumping was obtained. This motion provides the dominant contribution to the spin-lattice relaxation time above 40°C . In the temperature region from about 10°C to the ferroelectric transition temperature (-25°C to -35°C in the crystals studied) a high frequency motion, such as deuteron intrabond motion, was found to dominate the spin-lattice relaxation process. The activation energy for this motion was found to be 0.055 ± 0.01 eV. Below the ferroelectric transition, the deuteron spin-lattice relaxation time was found to be too short to be due to spin diffusion to paramagnetic impurities. This implied the presence of some molecular motion in which the deuterons are involved below the transition temperature, and a possible explanation was found in considering the contribution of torsional oscillations of SeO_3 groups to the spin-lattice relaxation time of the deuterons. The temperature and frequency dependence of the spin-lattice relaxation time of Na^{23} nuclei were similar to those of the deuterons over the same temperature and frequency ranges. The possibility of deuteron motion contributing to Na^{23} relaxation was therefore considered. In the 30°C to 80°C range, where deuteron interbond jumping is the dominant deuteron relaxation mechanism, it was found that the Na^{23} relaxation showed too small an activation energy (0.35 eV) to arise from deuteron interbond jumping. The indication of deuteron intrabond motion in the paraelectric phase is indicative of a dynamic order-disorder type ferroelectric phase transition. Evidence that the transition is not exclusively of this type, however, was found in the fact that the suppression of intrabond motion with the onset of polarization cannot explain the decrease in the deuteron spin-lattice relaxation time observed in the temperature region below the transition.

CHAPTER I: INTRODUCTION

The alkali trihydrogen selenite crystals are primarily of interest because of their dielectric properties.⁽¹⁾ Of the crystals in this family, the ferroelectric properties of sodium trihydrogen selenite ($\text{NaH}_3(\text{SeO}_3)_2$ hereafter abbreviated STSe) and the contrasting properties of the deuterated analogue of this crystal ($\text{NaD}_3(\text{SeO}_3)_2$ or DSTSe) are most unusual. At -79°C , STSe undergoes a transition of second order from its paraelectric α phase to a ferroelectric β phase.⁽²⁾ At -172.5°C , STSe exhibits another phase transition⁽³⁾ to a second ferroelectric γ phase. This transition exhibits a thermal hysteresis of 10.5°C and is therefore of first order. The paraelectric α phases of STSe and DSTSe are isomorphic but DSTSe exhibits only one phase transition, at -2.5°C ,⁽⁴⁾ to a ferroelectric phase^(5,6) which is apparently⁽⁷⁾ isomorphic to the lower ferroelectric γ phase of STSe. In DSTSe, there is no phase analogous to the β phase of STSe. These crystals are hydrogen-bonded, and the important changes in properties upon deuteration imply that the hydrogen-bonding plays an important role in the ferroelectric behavior.

Nuclear magnetic resonance (NMR) techniques have

proved useful in determining the electrical environment of nuclei with electric quadrupolar moments, and in detecting motions executed by various nuclei. The electric field gradients in a hydrogen bond can be studied by measuring the splitting of the deuteron Zeeman levels by the interaction of the deuteron's electric quadrupolar moment with the electric field gradient tensor. Changes in the electric environment of deuterons, and other nuclei with quadrupolar moments, such as Na^{23} , caused by ferroelectric phase changes, can be detected from NMR spectra of these nuclei. Furthermore, motions of nuclei, such as hindered rotations of molecular groups, single deuteron interbond and intrabond jumps, and random fluctuations of lattice modes of vibration may cause changes of magnetic fields or electric field gradients of the proper frequency to cause nuclear relaxation. Nuclear spin-lattice relaxation time measurements therefore provide a means of studying nuclear motions in crystals. For nuclei with $I > \frac{1}{2}$, an electric quadrupolar interaction is usually more effective in causing nuclear relaxation than is a magnetic dipolar interaction.

It was the intent of this investigation to study the environment and motions of hydrogens in a hydrogen-bonded material by NMR techniques. Sodium trihydrogen selenite

was chosen because of the possibility that some of the motions which might be detected could be related to the important ferroelectric properties of this material. Deuterated crystals were used because of the possibilities of additional information obtainable from interactions with the deuteron quadrupolar moment. Various experiments (to be discussed in the next chapter) have indicated that the phase transitions in STSe and DSTSe involve both ordering of the hydrogens and atomic displacement. Measurements of the NMR spectra of various nuclei (H^1 , H^2 , Na^{23}) in these crystals have been reported (8,9,10,11) and will be discussed in Chapter III. These studies provided additional clear evidence for the presence of both elements in the nature of the transitions. This investigation deals primarily with spin-lattice relaxation time (T_1) measurements and measurements intended to clarify the interpretation of the deuteron T_1 measurements, which are discussed in Chapters IV and V. They reflect the presence of deuteron interbond and intrabond motion in the temperature range between the melting point and the ferroelectric transition. Below the transition, no effects of interbond motion are observed, and the dominant mechanism for deuteron spin relaxation seems

to arise from lattice vibration fluctuations and/or SeO_3 motion rather than single particle (deuteron) motions.

This does not mean that all deuteron motion stops below T_c , but it indicates that other motions become more important than individual deuteron motions in causing spin-lattice relaxation below the phase transition temperature.

CHAPTER II: KNOWN PROPERTIES OF STSe and DSTSe

Three x-ray investigations of the crystal structure of STSe in the paraelectric phase have been made.^(3,11,12) Unterleitner claims that the space group of this phase is $P2_1/a$, class 2/m, while Chou and Tang* claim that the Na and Se atoms conform to space group $P2_1/a$ but to include the oxygens, the space group Pn, class m, is applicable. In $P2_1/a$, all SeO_3 are related by the symmetry operations of the space group, while they are not in Pn. (For comparison, $\text{LiH}_3(\text{SeO}_3)_2$ is of class m, and two types of SeO_3 groups have been identified by Pepinsky and Vedam⁽²⁾ in this crystal.) Detailed structural analyses of the lower temperature phases to locate all atomic positions have not been made on STSe, but approximate cell dimensions and symmetries have been determined. These results, based primarily on Unterleitner's work**, are summarized in Tables I and II. To date, no structure studies have been done on either phase of DSTSe, but the paraelectric phase is

*This translation of Ref. 11 is from Roger P. Kohin, Clark University, Worcester, Mass.

**Anderson(9) found that these results were more consistent with the directions of O—H...O bonds implied by his efg tensor measurements of deuteron sites than the results of Chou and Tang.

TABLE I: CELL PROPERTIES OF $\text{NaH}_3(\text{SeO}_3)_2$

	Paraelectric Phase T > -79°C	Ferroelectric Phase I -79°C to -172°C	Ferroelectric Phase II T < -172°C
Crystal Symmetry	Monoclinic 2/m	Triclinic 1	Monoclinic m
Space Group	P 2 ₁ /c	C	
a cell dimension	10.36 Å	20.60 Å	10.4 Å
b cell dimension	4.84 Å	9.57 Å	9.57 Å
c cell dimension	5.80 Å	5.76 Å	5.75 Å
Cell angle	90°	89°36'	90°
Cell angle	91°10'	91°	
Cell angle	90°	90°18'	90°

TABLE II: ATOMIC COORDINATES

(Dimensions in Fractions of Unit Cell Dimensions)

Atom	x	y	z
Na	0.0	0.0	0.500
Se	0.170	0.380	0.0
O _I	0.051	0.159	0.860
O _{II}	0.145	0.281	0.290
O _{III}	0.301	0.185	0.951

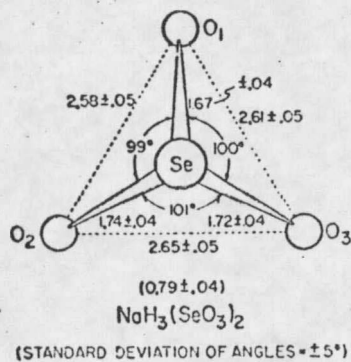


Figure 1: SeO₃ Pyramid in NaH₃(SeO₃)₂
(after Vedam, Okaya, & Pepinsky⁽²⁾)

assumed to have the same symmetry, space group, and interatomic distances as the α phase of STSe. Most evidence indicates that the structure of the lower temperature phase of DSTSe is similar to that of the γ phase of STSe.

Figures 2 and 3 illustrate the hydrogen-bonding of the crystal. Of the three hydrogen bonds per molecule, two (N and N', Fig. 2 - length $2.56 \text{ \AA}$) are identical. This is not evident from the figure but is from the x-ray studies and NMR spectra. The third bond (S - length $2.61 \text{ \AA}$) is special in that its center is also a center of symmetry in the unit cell. We therefore use the following designations in referring to the two types of bonds:

TABLE III: BOND PROPERTIES (PARAELECTRIC PHASE)

length, $\text{\AA}$	designation	number/cell
2.56	N (non-symmetric)	4
2.61	S (symmetric)	2

From Fig. 3, it is evident that there are physically two types of N bonds and two types of S bonds, each having different directions. From x-ray studies by Pepinsky,⁽²⁾ or from the atomic coordinates listed in Table 2, the dimensions of the SeO_3 pyramid are obtained. Fig. 1 summarizes these interatomic parameters.

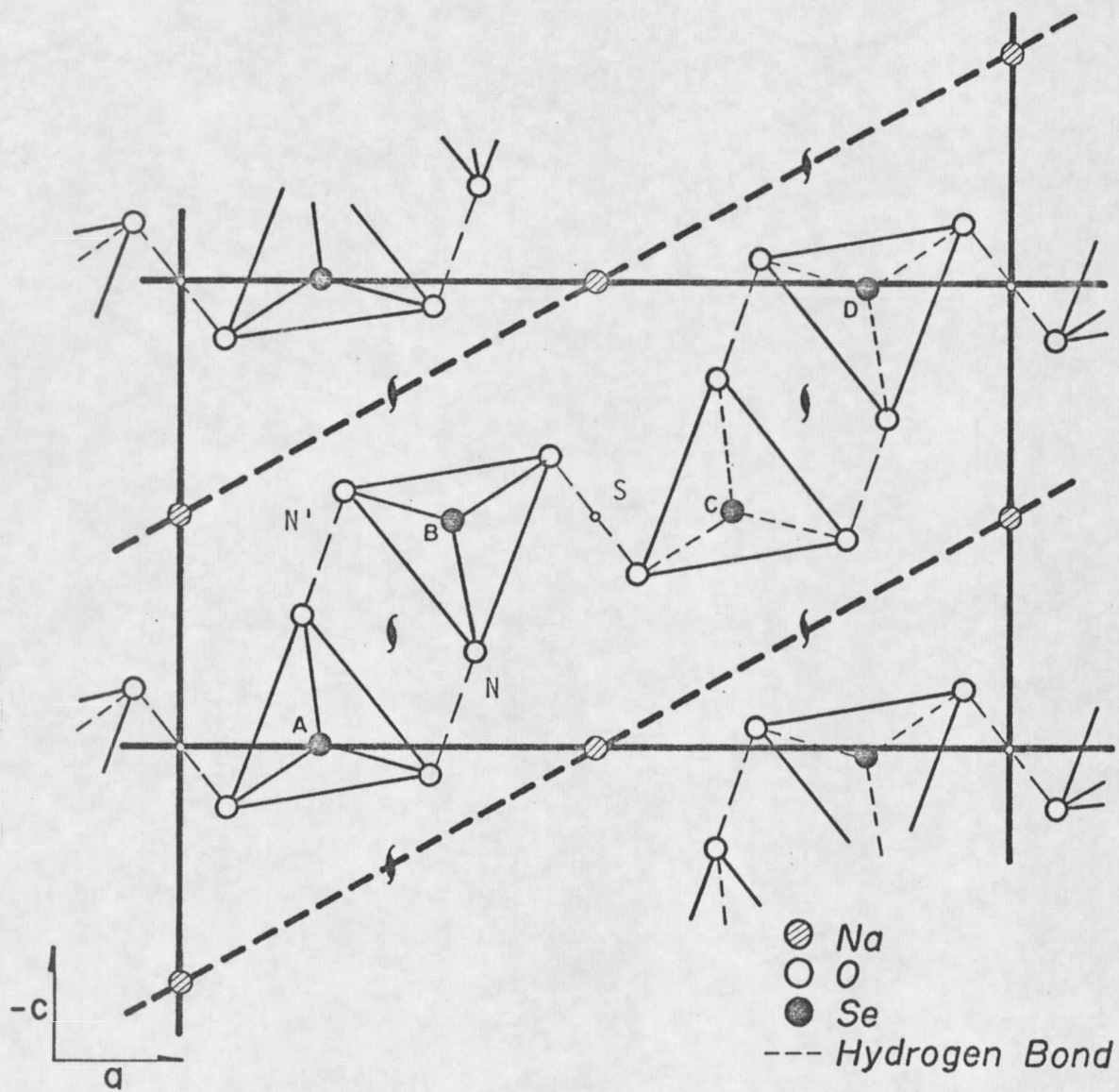


Figure 2: a, c Projection of Unit Cell
of $\text{NaH}_3(\text{SeO}_3)_2$ (after Cvikl⁽⁸⁾)

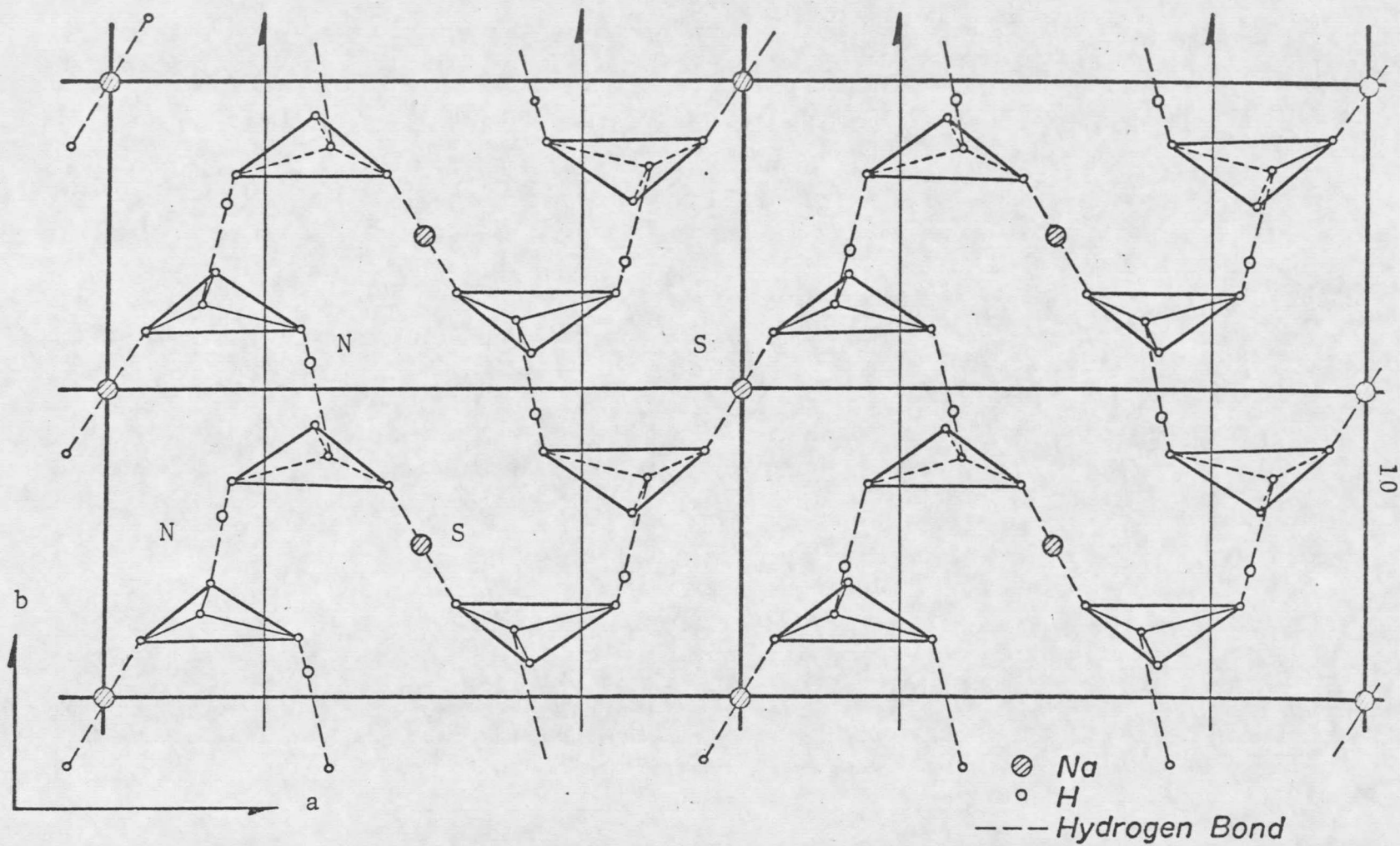


Figure 3: a,b Projection of 4 Unit Cells of $\text{NaH}_3(\text{SeO}_3)_2$ (after Cvinkl⁽⁸⁾)

No neutron studies of either STSe or DSTSe have yet been reported so the locations of the hydrogen atoms have not yet been determined by direct measurement. However, some NMR measurements, discussed in the next chapter, give unambiguous evidence about which oxygens are connected through hydrogen bonds and indicate the probable localization of hydrogen in bonds.

Crystals of various concentrations of deuterium have been studied by various workers,^(3,4,5,6,13,14) mostly in connection with the measurement of dielectric and ferroelectric properties. It is generally agreed that the structure of the paraelectric phase is the same, regardless of deuterium concentration. It is further agreed^(4,13) that the dependence of the transition temperature on concentration is a hyperbolic function, as discussed by Janovec.⁽¹⁵⁾ In undeuterated crystals, Makita⁽¹⁶⁾ was first to report a third γ phase, also ferroelectric. Makita and Zherebtsova and Rostuntsova⁽¹³⁾ report its onset at $94 \pm 4^\circ\text{K}$ while Ivanov et al⁽³⁾ report that upon warming, it occurs at 111°K , and upon cooling, the transition occurs at 100.5°K . Polarization in the intermediate β phase is both along the xz plane (different authors pick these two axes differently) and along the y axis. The presence of polarization along the y axis rules out monoclinic sym-

metry: the crystal symmetry in this phase is believed to be triclinic 1. Both Russian groups agree^(3,13) that it is likely that the polarizations along the y axis and in the xz plane are due to different mechanisms. Ivanov⁽³⁾ suggests that the xz polarization is due to proton ordering while the y polarization, although probably triggered by proton rearrangement, is due to Na⁺ displacement along the y axis. In the lower phase, the y axis polarization disappears and in some crystals,⁽¹³⁾ all polarization disappears. Ivanov and Shuvalov⁽³⁾ find that for the γ phase, the symmetry reverts to monoclinic, this time of system m. As deuterons are added, Zherebtsova and Rostuntsova⁽¹³⁾ claim that the temperature of the $\beta \leftrightarrow \gamma$ transition goes down. Their experimental observations consist of the observation of this transition at 94°K for 10% deuteration. They apply a hyperbolic dependence of the transition temperature on concentration to these results and illustrate the results in the diagram of Fig. 4. This indicates that the β phases of STSe and DSTSe are analogous and that the γ phase is no longer present above 55% deuteron concentration. However, Shuvalov et al.⁽⁶⁾ find that the lower phase of completely deuterated DSTSe is monoclinic of class m which would make the lower phase of DSTSe analogous to the γ phase of STSe. The β phase of

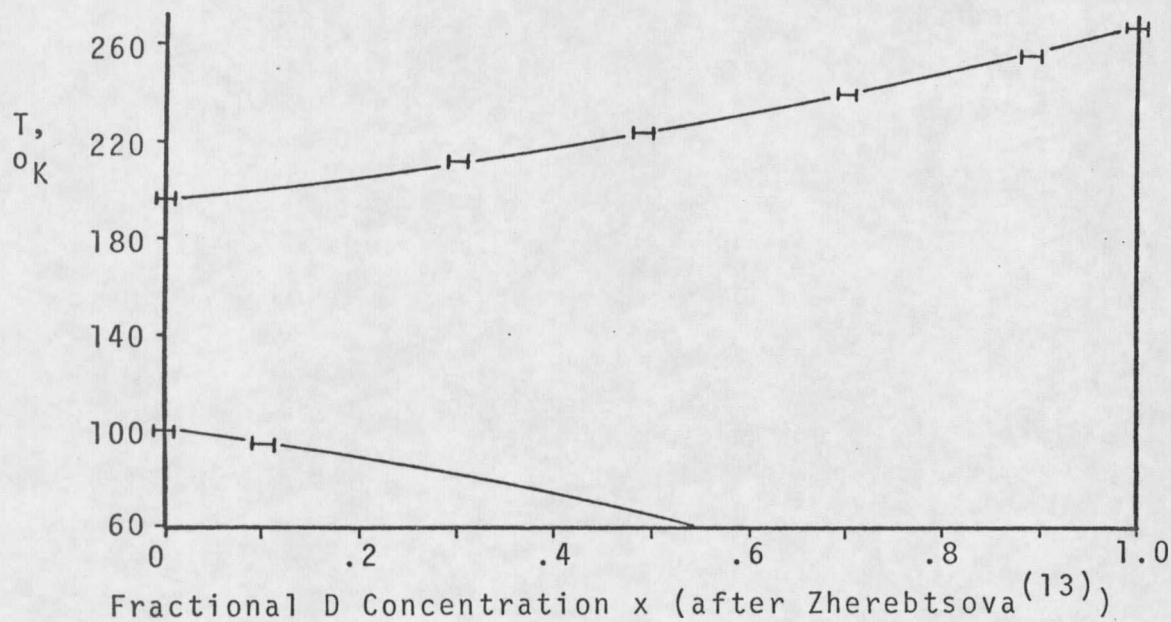


Figure 4: $\text{Na}(\text{H}_{(1-x)}\text{D}_x)_3(\text{SeO}_3)_2$ Phase Diagram

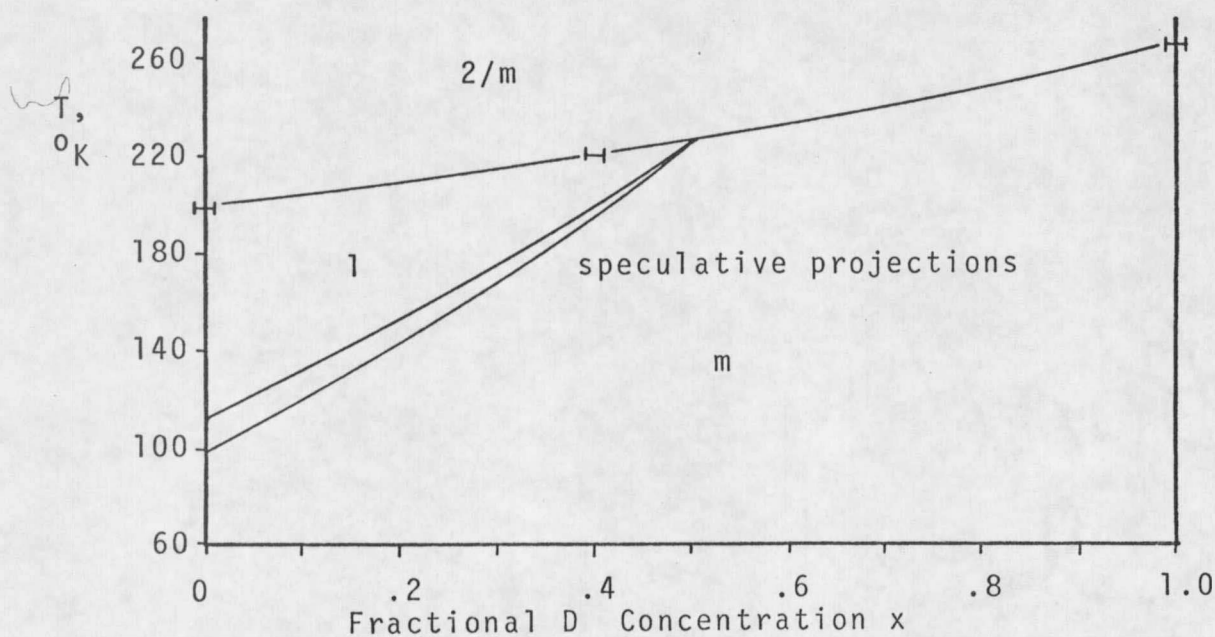


Figure 5: $\text{Na}(\text{H}_{(1-x)}\text{D}_x)_3(\text{SeO}_3)_2$ Phase Diagram

triclinic structure is, according to their study, the phase which is absent in crystals of high deuterium concentration. Their results are sketched in principle in Fig.

5: the exact location of the $m \leftrightarrow 1$ phase boundary is not known.

When the first thorough study of the dielectric and ferroelectric properties of DSTSe was published, Blinc et al.⁽⁵⁾ interpreted the observance of double hysteresis loops in the lower phase as evidence of an antiferroelectric state. Added to the shift in transition temperature, this difference would make the effect of deuteration very remarkable. More recently, however, because of the observation of a shift in transition temperature with high applied field, Blinc et al.⁽⁷⁾ have indicated that this transition may actually be ferroelectric. Furthermore, Shuvalov et al.⁽⁶⁾ have recently reported the observation of normal hysteresis loops in fresh crystals of DSTSe, and therefore conclude that double hysteresis loops, which they also observe in older crystals, are results of ageing effects, not of an antiferroelectric state. In STSe, the $\alpha \leftrightarrow \beta$ transition is second order while the $\beta \leftrightarrow \gamma$ transition is first order, on the basis of the presence or absence of thermal hysteresis. For the transition of DSTSe,

however, Shuvalov et al.⁽⁶⁾ list several indications of a second order transition.

For comparison, the basic ferroelectric properties of the other alkali trihydrogen selenites and ammonium trihydrogen selenite are summarized in Table IV. Unlike STSe, potassium, rubidium and cesium trihydrogen selenites exhibit only one phase transition, lithium trihydrogen selenite retains its ferroelectric phase until it melts at 111°C , and ammonium trihydrogen selenite shows no ferroelectric or antiferroelectric phase. Work done in this laboratory by Kenneth Hsu⁽¹⁷⁾ indicates that deuteration of KTSe and CTSe raises the transition temperature of these materials: discontinuities in the slopes of the dielectric constant were observed in DKTSe at 3°C and in DCTSe at -100°C . The percent deuteration in these crystals has not yet been measured, but is believed to be 60 to 85%. These measurements, together with those of other workers summarized in Table IV, imply that the hydrogen bonds play an important role in the ferroelectric properties of at least potassium and cesium trihydrogen selenites, as well as in sodium trihydrogen selenite.

Infrared absorption studies on STSe and DSTSe have been reported by several groups. From a spectrum at room temperature in the $55 - 170 \text{ cm}^{-1}$ range, Myasnikova and

TABLE IV: SOME FERROELECTRIC PROPERTIES OF
ALKALI AND AMMONIUM TRIHYDROGEN SELENITES

	Transition Temperature	Nature of Lower Temperature Phase	Crystal Class
$\text{LiH}_3(\text{SeO}_3)_2^{(18)}$	--	Ferroelectric to 110°C melting point	m
$\text{LiD}_3(\text{SeO}_3)_2$	--	Ferroelectric to 110°C melting point	m
$\text{KH}_3(\text{SeO}_3)_2^{(19)}$	-62.5°C	Antiferroelectric	$\text{mmm} \leftrightarrow 1$ or $\bar{1}$
$\text{KD}_3(\text{SeO}_3)_2^{(20)}$	$+24^\circ\text{C}$		
$\text{RbH}_3(\text{SeO}_3)_2^{(1)}$	-114°C	Ferroelectric	$222 \leftrightarrow 2$
$\text{CsH}_3(\text{SeO}_3)_2^{(21)}$	-128°C	Probably anti- ferroelectric	$\bar{1} \leftrightarrow \bar{1}$
$\text{CsD}_3(\text{SeO}_3)_2$	$>100^\circ\text{C}$		
$\text{NH}_4\text{H}_3(\text{SeO}_3)_2$	--	Paraelectric only	222

Arefev⁽²²⁾ observed four absorption bands, at 57, 74, 80, and 113 cm^{-1} . The intent of their study was to observe a ferroelectric mode but they do not specifically associate any of these absorptions with any particular type of motion. From a study of STSe in the 600 cm^{-1} to 3000 cm^{-1} range, Blinc and Pintar⁽²³⁾ identified broad OH stretching bands at 2750 cm^{-1} and at $2200 - 2400\text{ cm}^{-1}$ and OH deformation bands at 1580 cm^{-1} and at $1000 - 1230\text{ cm}^{-1}$. The $2200 - 2400\text{ cm}^{-1}$ band appeared to be split, and the splitting increased in the ferroelectric state. No large shifts in the spectra were observed on passing to the ferroelectric state. In a study over the 300 to 4000 cm^{-1} range, Khanna, Decius, and Lippencott⁽²⁴⁾ have identified many SeO_3 and hydrogen bond absorption lines in STSe and DSTSe at room temperature and at 77°K . They observed absorptions characteristic of SeO_3^- bending and stretching vibrations at room temperature and absorptions characteristic of HSeO_3^- and H_2SeO_3 vibrations at 77°K .

Makita^(25,26) has measured the specific heat anomalies of the phase transitions in STSe and DSTSe and has obtained the transition energies and entropy changes given in Table V. For a purely order-disorder transition, the entropy change, δS , should equal $R \ln 2$ or $1.37\text{ cal/mole}^\circ\text{K}$.

The observed values are close enough to be consistent with such a transition, but the discrepancies from this value also imply the presence of additional causes, such as some atomic displacements in the transitions.

TABLE V: TRANSITION ENERGIES AND ENTROPY CHANGES
IN PHASE TRANSITIONS OF $\text{NaH}_3(\text{SeO}_3)_2$ AND $\text{NaD}_3(\text{SeO}_3)_2$

	Transition Energy cal/mole	Entropy Change cal/mole $^{\circ}\text{K}$
$\text{NaH}_3(\text{SeO}_3)_2$	201 ± 9	$1.03 \pm .05$
	47 ± 8	0.5 ± 0.1
$\text{NaD}_3(\text{SeO}_3)_2$	274 ± 27	1.0 ± 0.1

From this discussion of previous studies of DSTSe and STSe, certain evidence (the near agreement between experimental and order-disorder theoretical values of δS at the transition and the splitting but lack of significant shift in OH stretching and deformation frequencies) implies the presence of proton ordering in the ferroelectric state, while other evidence (doubling of the unit cell size and slight deviations of the experimental value of δS from that predicted by order-disorder theory) imply atomic displacement in the phase transitions of STSe. In the following chapter, additional conclusive evidence for the

presence of both elements in the ferroelectric mechanism of STSe and DSTSe will be discussed.

CHAPTER III: NMR SPECTRA IN STSe AND DSTSe

Studies of the line width of the proton NMR signal in STSe have been made by several people. Blinc and Pintar (23) observed a small increase in the second moment of the proton line as the first ferroelectric state is attained. This change is consistent with a change from a dynamically disordered to an ordered proton arrangement. The magnitude of this change in second moment is linear with proton concentration, (27) implying that upon partial deuteration, deuterons populate all types of bonds with equal probability.* The angular dependence of the second moment of the proton line was also studied by Gavrilova-Podol'skaya et al. (28) By using the positions of the other atoms as determined by x-ray studies and assuming reasonable positions for the protons (only O—H...O bonds shorter than $3.5 \text{ \AA}$ were assumed), the orientational dependence of the second moment was calculated for three different assumed sets of proton locations. Good agreement with experiment

* It will be shown later, that at room temperature and above, there is substantial evidence that deuterons exchange sites. Since crystals are generally grown in this temperature range, the linearity of the second moment of the proton line with proton concentration should therefore be interpreted as evidence of the dynamical concentration of protons and deuterons being equal in all sites.

was obtained only for a model in which every oxygen partakes in one hydrogen bond. This set was not the same set which is illustrated in Fig. 2, however. Instead of connecting SeO_3 groups in planes along the $[10\bar{1}]$ direction, as in Fig. 3, the set of bonds proposed in Ref. 28 connect SeO_3 groups in planes parallel to the $[001]$ direction. These connect planes of SeO_3 groups in which all Se atoms are on the same sides (relative to the b axis) of their planes of oxygen atoms. To calculate the second moment of the proton line, for each set of bonds, it was assumed that each proton is midway between the oxygen atoms of the bond.

The^a nuclear magnetic resonance spectra of deuterons in DSTSe were studied by Anderson,⁽⁹⁾ by Cvikl,⁽⁸⁾ and by Blinc and Zupancic.⁽¹⁰⁾ The Na^{23} spectra in both STSe and DSTSe were studied by Zupancic, Blinc, and coworkers,^(5,7,29) and by Soda and Chiba.⁽³⁰⁾ Both H^2 and Na^{23} have electric quadrupolar moments which interact with the electric field gradients of the local environment. Since the effect of this electric quadrupolar interaction on the magnetic Zeeman levels of the nucleus is prerequisite to the discussion of spin-lattice relaxation time measurements in the subsequent chapters, a discussion of this

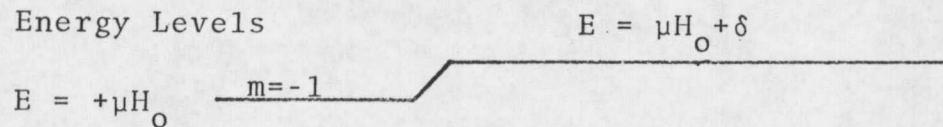
effect will be given here for the case of deuterons. A more detailed development of the interaction is to be found in the literature. (31,32)

The energy level diagram of the spin 1 deuteron due to a magnetic field, H_0 , is three equally spaced levels (Zeeman levels) of energy separation μH_0 . The transitions between the two pairs of levels ($-\frac{1}{2} \leftrightarrow 0$ and $0 \leftrightarrow +\frac{1}{2}$) are therefore at the same frequency, $\nu_0 = \mu H_0/h$, called the Larmor frequency. The effect of the interaction of the deuteron electric quadrupolar moment with the electric field gradient is to shift the Zeeman levels slightly (Fig. 6), dividing the single absorption line at ν_0 into two lines at frequencies $\nu_0 \pm \Delta\nu$. For the magnetic field strengths (7 - 22 kilogauss) used in the experiments discussed here, the quadrupolar splitting of the Zeeman levels may be accurately treated as a first order perturbation. The splitting ($2\Delta\nu$) is independent of the magnetic field in this approximation and is given by

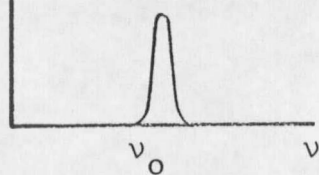
$2\Delta\nu = K\phi_{z,z}$, where $\phi_{z,z}$ is the electric field gradient tensor component which is along the applied magnetic field and the constant $K = 3eQ/2h$, where e is the deuteron charge and Q is the deuteron electric quadrupole moment.

By measuring the deuteron NMR spectrum as a function of angle for rotations about three mutually perpendicular

Energy Levels

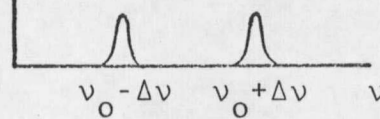


I | Zeeman Splitting



$$\nu_0 = \frac{\mu H_0}{h}$$

I | Zeeman & Quadrupolar Splitting



$$\text{separation } 2\Delta\nu = \frac{2\delta}{h} = K\phi_{z'z'}$$

Figure 6: Splitting of Nuclear Zeeman Levels
by the Quadrupolar Action for $I = 1$

axes, the electric field gradient in the coordinate system of these three axes is obtained. By diagonalizing this tensor, one obtains the efg components in the principal coordinate system and the direction cosines between the principal components and the axes of rotation. (A convenient formulation of this problem has been given by Volkoff, Petch and Smellie.⁽³¹⁾)

The angular dependence of the quadrupolar splitting was measured for rotations about three mutually perpendicular axes. These axes, illustrated in Fig. 7, were chosen because the prominent faces of the particular crystal studied made alignment along these axes convenient. For rotations about X, Y, and Z, the symbols θ_X , θ_Y , and θ_Z are used. These represent the angles between Y and H_0 , Z and H_0 , respectively. The laboratory reference frame (x' , y' , z') is also right handed, with z' along the applied magnetic field H_0 , and with y' coinciding with the crystal axis (X, Y, or Z) of rotation. The angles refer to counter-clockwise rotations of the crystal frame (X, Y, Z) with respect to the laboratory frame (x' , y' , z'). The splitting $2\Delta\nu$ is plotted as a function of angle in Figs. 8 and 9. It is customary to express the efg components of the principal system as $K\phi_{xx}$, $K\phi_{yy}$, and $K\phi_{zz}$ in units of

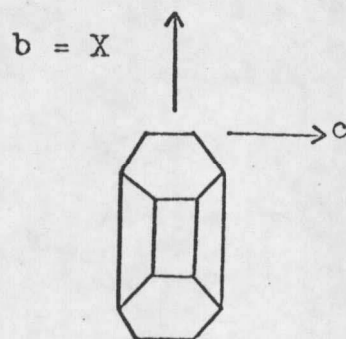
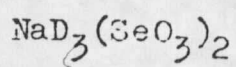
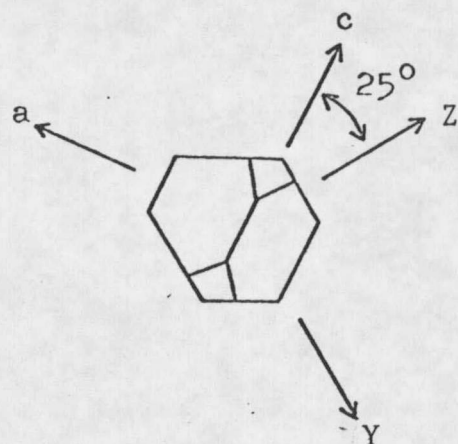


Figure 7: Relationship of Rotation Axes
to Crystalline Axes

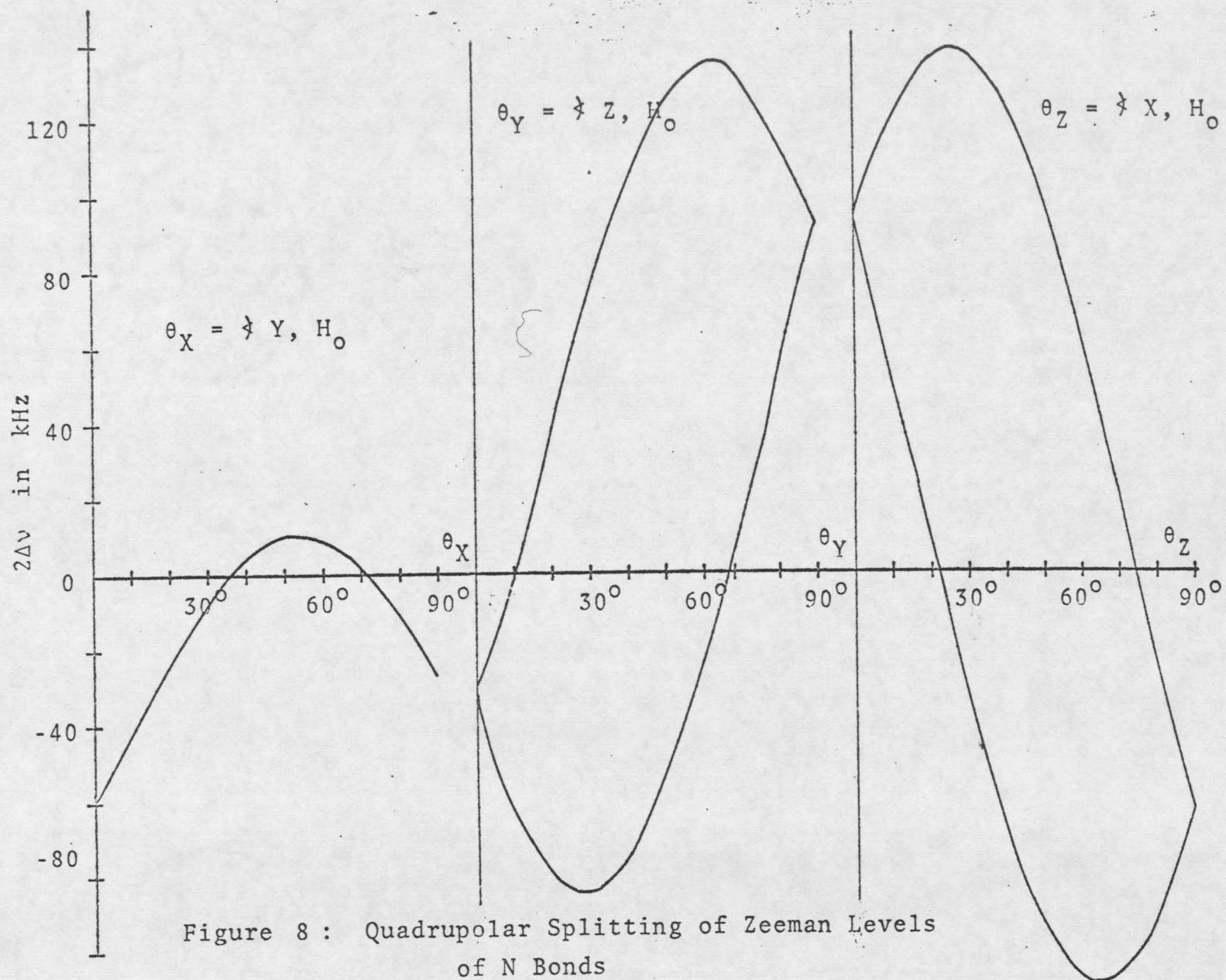


Figure 8 : Quadrupolar Splitting of Zeeman Levels
of N Bonds

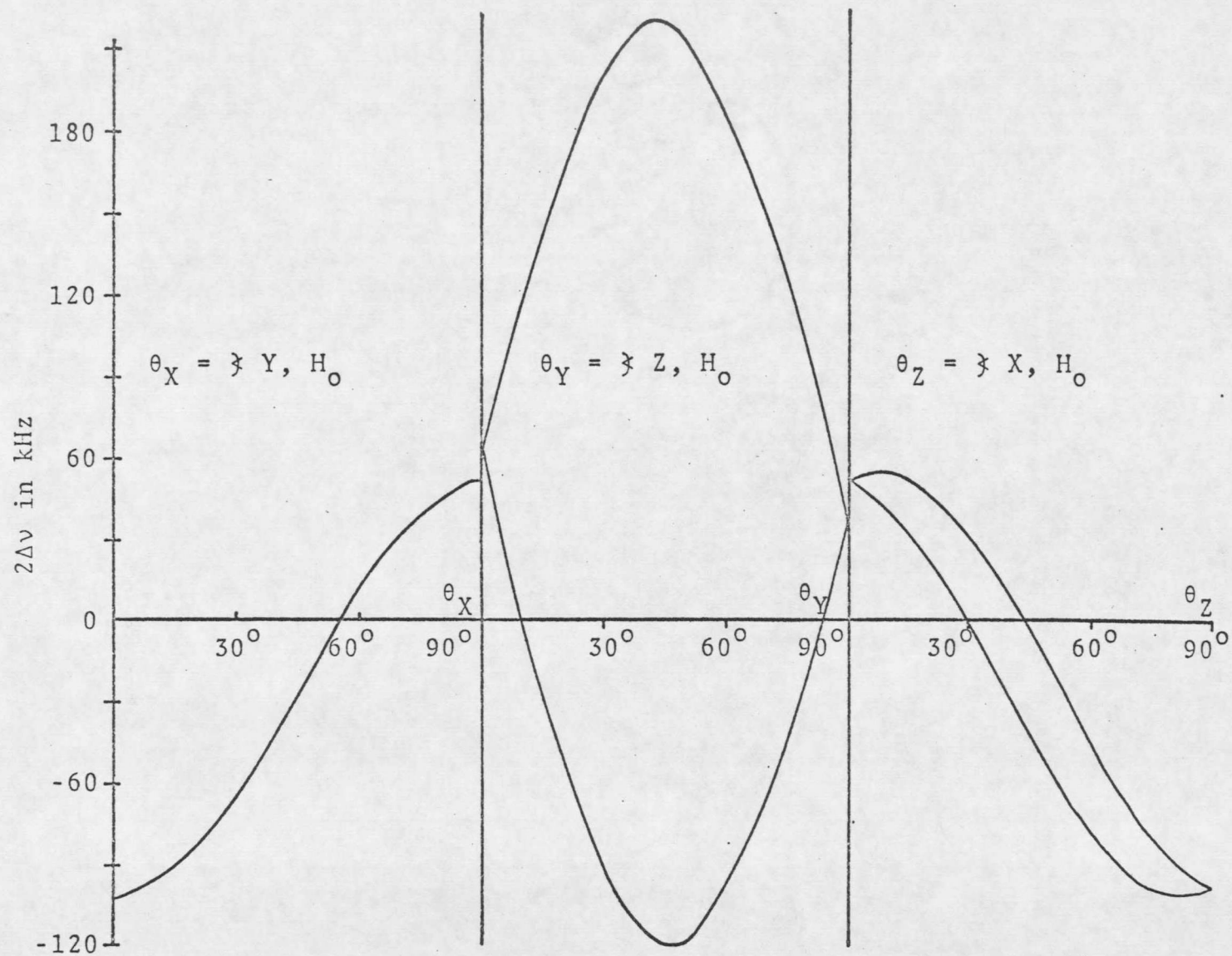


Figure 9: Quadrupolar Splitting of Zeeman Levels of S Bonds

kiloHertz, choosing $|K\phi_{xx}| < |K\phi_{yy}| < |K\phi_{zz}|$, and to assign a positive sign to $K\phi_{zz}$. Since these components satisfy Laplace's equation, the three numbers can be summarized in terms of the two parameters $e^2qQ/h = (2/3)K\phi_{zz}$ (designated the quadrupolar coupling constant) and $\eta = (\phi_{xx} - \phi_{yy})/\phi_{zz}$ (designated the asymmetry parameter). The results obtained from this data are given in Table VI.

TABLE VI: ELECTRIC FIELD GRADIENT COMPONENTS
OF DEUTERON BONDS IN DSTSe AT 25°C

	N bonds	S bonds
$\frac{eQ\phi_{zz}}{h}$	$124 \pm 7 \text{ kHz}$	$146 \pm 9 \text{ kHz}$
η	0.15 ± 0.04	0.19 ± 0.04
$K\phi_{xx}$	$-80 \pm 5 \text{ kHz}$	$-89 \pm 5 \text{ kHz}$
$K\phi_{yy}$	$-107 \pm 6 \text{ kHz}$	$-131 \pm 8 \text{ kHz}$
$K\phi_{zz}$	$+186 \pm 11 \text{ kHz}$	$+220 \pm 13 \text{ kHz}$

Since the studies of Anderson⁽⁹⁾ and Blinc⁽¹⁰⁾ became available shortly after these measurements were made, further studies of the deuteron splitting in the ferroelectric phase were unnecessary. From these studies, and the later work by Soda and Chiba, several conclusions were drawn.^(29,30)

a. Above T_c , the direction cosines of the ϕ_{zz} components are consistent (within 1° for the N bonds and within 5° for the S bonds) with the 0 - 0 directions determined

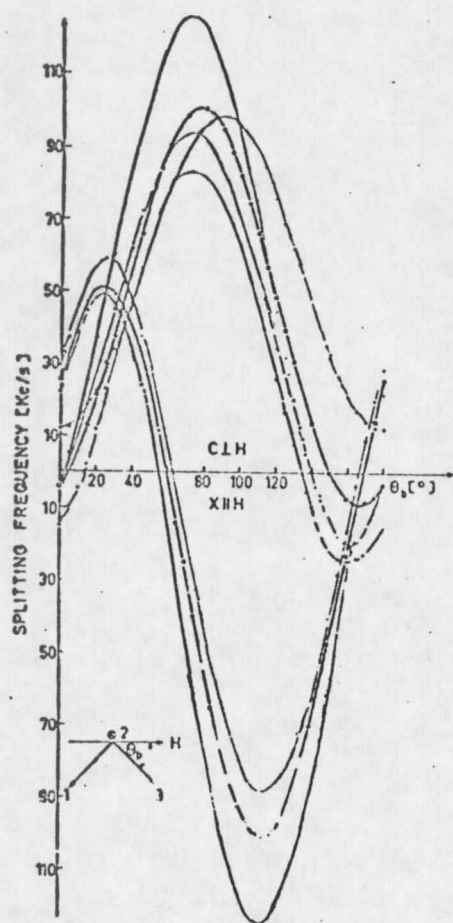
from x-ray studies⁽¹²⁾ of STSe. Since the direction of the largest principal efg component is generally along the 0 - 0 bond direction,⁽³³⁾ this result confirms the isomorphism of the paraelectric phases of DSTSe and STSe.

b. Above T_c , the direction cosines of the second largest principal efg components are roughly between the normals to the Se—O...O' and O...O'—Se' planes, indicating that the deuteron, within a time equal to the inverse of the splitting frequency, sees an average effect of the two SeO_3 to which it bonds.

c. Below T_c , the deuteron bonds distort into six chemically inequivalent types. A b axis rotation (Fig. 10) illustrates the resulting deuteron NMR spectra. This implies that the cell size doubles so that two kinds of S and two kinds of N bonds result and it also indicates that the two N bonds per cell which were equivalent now are no longer equivalent.

d. The direction cosines of the ϕ_{zz} components, and the coupling constants and asymmetry parameters, do not change very much, which indicates that, while some atomic displacement occurs at the transition, no great changes in the bonds occur.

e. Below T_c , the direction cosines of the second largest principal components roughly coincide with the normals to



b rotation

Paraelectric Phase

$T = 293^{\circ}\text{K}$

Ferroelectric Phase

$T = 236^{\circ}\text{K}$

Figure 10: $\text{NaD}_3(\text{SeO}_3)_2$ Deuterium

Quadrupole Perturbed NMR (after Blinc⁽¹⁰⁾)

Se—O...O' planes, indicating that, during a time of the order of the inverse of the splitting frequency, the electrical environment of a deuteron is determined by one SeO_3 tetrahedron. This is consistent with a deuteron bond model having two equilibrium sites for the deuteron in a bond above T_c , with the deuteron moving back and forth between the two sites rapidly (with frequency $>$ splitting frequency), while below T_c the deuterons order in preferred equilibrium sites.

From their deuteron NMR rotation spectra below the transition, each group (Blinic, Stepisnik and Zupancic⁽²⁹⁾ and Soda and Chiba⁽³⁰⁾) has proposed an arrangement of deuterons in preferred ends of bonds. These assignments disagree on which is the preferred end of the bond for one type of N deuteron. Both studies were done well below the transition temperature (Blinic at 153°K, Soda at 134°K) and both arrangements agree with the proposed symmetry and size of the unit cell which has been confirmed by other measurements. At present there is no other evidence to distinguish between these two cases. Schmidt⁽³⁴⁾ has observed that seven additional possibilities of deuteron arrangements on preferred ends of bonds exist. These also contain only D_2SeO_3 and DSeO_3^- groups in addition to Na^+ ions, are reversible,

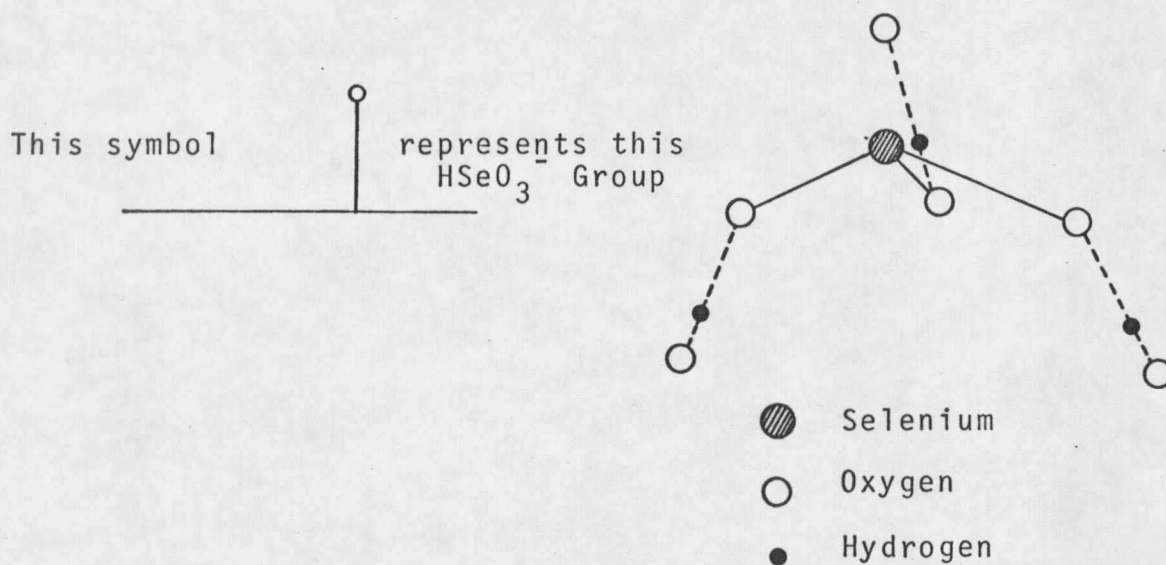
and are consistent with the symmetry of the m class and Pn space group. These nine possibilities are summarized in Table VII, using the notation defined in Fig. 11. The ordered arrangement of deuterons proposed by Blinc et al.⁽²⁹⁾ is given in Fig. 12 to further clarify the notation of Table VII.

The groups of Blinc^(7,29) and Soda⁽³⁰⁾ also made similar studies of the quadrupolar perturbation for Na^{23} in all phases of both STSe and DSTSe. The results are summarized as follows:

a. In both STSe and DSTSe, above T_c , there are two physically inequivalent Na^{23} sites related by a mirror plane. These two sites are chemically equivalent. Coupling constants, asymmetry parameters, and direction cosines in the two crystals are in close enough agreement to imply isomorphic states.

b. Below the first transition, Na^{23} lines in STSe split into four lines, indicating four times as many inequivalent sites and doubling of unit cell dimensions in two directions.

c. In the lower phase of DSTSe and the second ferroelectric (γ) phase of STSe, there are twice as many Na^{23} lines as in the paraelectric states, indicating a doubling of unit cell size in only one direction in those states.



Letter Representation of Possible HSeO_3^- and H_2SeO_3 Groups

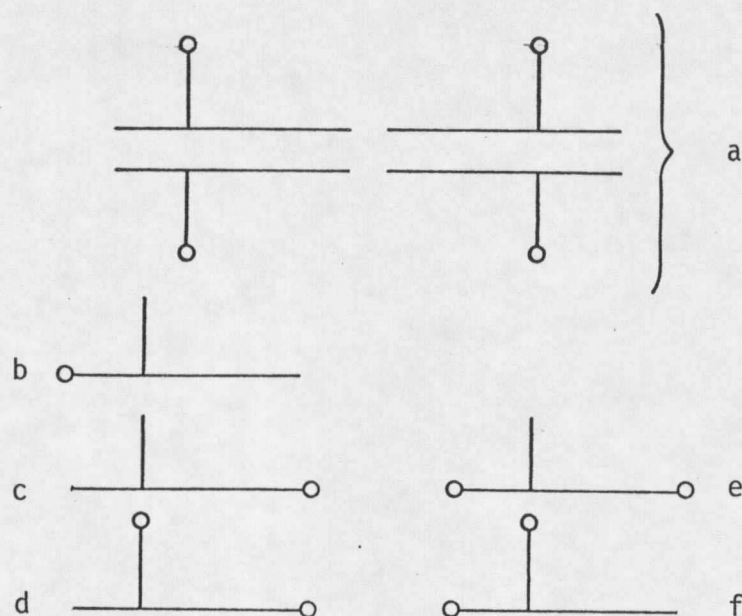


Figure 11: Simplified Notation for HSeO_3^- and H_2SeO_3 Groups

TABLE VII: POSSIBLE ARRANGEMENTS OF HSeO_3^- AND H_2SeO_3 GROUPS*

I.	a	a	II.	a	a	III.	b	b
	f	d		b	d		b	f
	b	b		f	f		f	f
	d	f		d	b		f	b
IV.	a	a	V.	b	b	VI.	c	c
	f	c		f	a		a	e
	d	d		d	d		d	d
	c	f		a	f		e	a
VII.	a	a	VIII.	b	b		c	c
	d	c		d	a		c	e
	e	e		e	e		e	e
	c	d		a	d		e	c

*

The notation used here is defined in Figure 11. Arrangement I is the one assigned by Soda and Chiba⁽³⁰⁾ and arrangement VIII is the one assigned by Blinc et al.⁽²⁹⁾

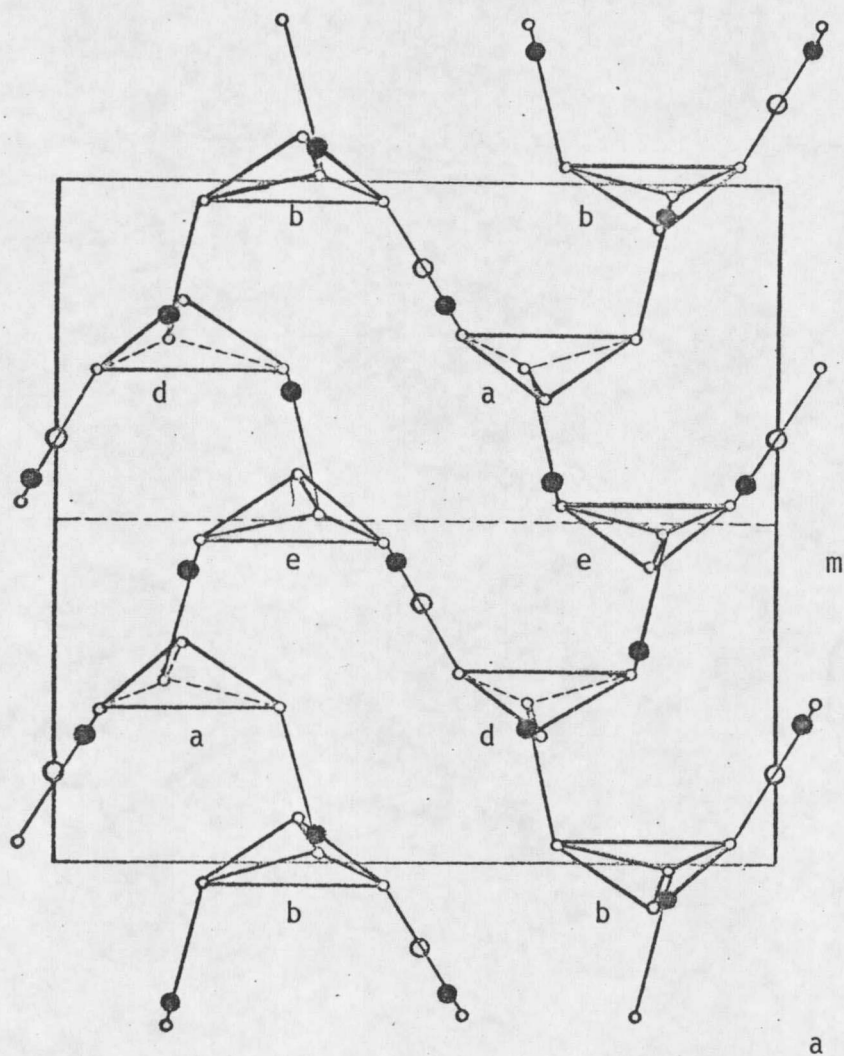


Figure 12: a, b Projection of a Unit Cell
Ferroelectric $\text{NaD}_3(\text{SeO}_3)_2$ (after Blinc et al. ⁽²⁹⁾)

Again, the coupling constants, asymmetry parameters, and direction cosines are sufficiently similar to imply isomorphic states. Two sites are electrically similar to those of the paraelectric state, while the other two sites show much greater asymmetry as well as other changes.

For future reference, values of the effective charges used to manufacture the room temperature Na^{23} efg tensor values via a point charge model are given in Table VIII. The Sternheimer anti-shielding factor $(1 - \gamma_\infty)^{(35)}$ was 6. (29)

TABLE VIII: EFFECTIVE IONIC CHARGES
FOR FITTING Na^{23} EFG TENSOR IN $\text{STSe}^{(29)}$

Na	1.0 e	(e = 1 positive electronic charge)
Se	1.1 e	
O	-1.0 e	
H	0.9 e	

CHAPTER IV: DEUTERON MOTION ABOVE T_c

SECTION I: Electrical Conductivity

Many hydrogen-bonded solids have been shown to be semiconductors and in many cases, including ice,⁽³⁶⁾ potassium dihydrogen phosphate⁽³⁷⁾ and lithium hydrazinium sulphate,⁽³⁸⁾ direct coulometric measurements have indicated that protons are the carriers in these materials. The electrical conductivity of STSe and DSTSe was measured for samples of single crystals of these materials cut so that electric fields could be applied along the respective crystalline axes. The technique used for these measurements is described in Chapter VII. The results of these measurements are given in Table IX. Over the temperature range for which the given activation energies are valid, the conductivity changed by four to five orders of magnitude. The activation energies and pre-exponential factors (σ_0) were obtained by a least squares fit to the experimental points. Uncertainty in fitting these points is negligible - the largest errors in these measurements arise from uncertainties in the thickness (1%) and contact area (4%) measurements for the individual samples and in varying quality of individual crystals. The magnitude of this

TABLE IX: ELECTRICAL CONDUCTIVITY ABOVE T_c

	Crystal Axis	Temperature Range °K	E(eV)	σ at 25°C (ohm-cm) ⁻¹	σ_0 (ohm-cm) ⁻¹
NaH ₃ (SeO ₃) ₂	a	253 to 323	0.76	4.3×10^{-9}	2.8×10^4
	b	270 to 322	0.74	1.2×10^{-9}	4.0×10^3
	c	222 to 294	0.82	5.4×10^{-9}	3.8×10^5
NaD ₃ (SeO ₃) ₂	a	253 to 328	0.79	3.2×10^{-9}	3.9×10^4
	b	263 to 351	0.74	9.3×10^{-9}	1.9×10^3
	c	256 to 328	0.79	5.4×10^{-9}	1.1×10^5

latter effect is difficult to estimate reliably.

The samples of DSTSe were cooled to below their transition temperatures. Upon passing through the transition, the crystals cracked but did not crumble, so the crystals were cooled further, until the conductivity became too small to be measureable. Discontinuous jumps in the conductivity occurred in about a 20°C range below the transition, but in all cases, the conductivity again became exponential with temperature. The activation energies in this temperature range are more varied than those obtained above the transition (Table X). The results in this temperature range were not particularly meaningful, however, because cracks in the crystal form paths for surface conduction, allowing the same inherent errors as a measurement of the conductivity without using a guard ring.

TABLE X: ELECTRICAL CONDUCTIVITY BELOW T_c

Axis	Range	Activation Energy
a	238°K to 222°K	0.60 eV
b	218°K to 194°K	0.66 eV
c	247°K to 192°K	0.53 eV

SECTION II: Spin-lattice Relaxation Time of Deuterons

The term "spin-lattice relaxation time" (designated T_1) refers to the time which is characteristic of the return of nuclei in a magnetic field to a Boltzman distribution (of the spins in their allowed energy levels) at the lattice temperature, when this thermal equilibrium has somehow been disturbed. Many and various processes, causing both electrical (if the nuclear spin has an electric moment) and magnetic interactions can contribute to this relaxation*. For example, any random deuteron motion which includes change of electric field gradient tensor components as the deuteron moves from location to location can contribute to spin-lattice relaxation: there is an interaction between the deuteron quadrupolar moment and those efg tensor fluctuations which occur at the $\Delta m = 1$ and $\Delta m = 2$ transition frequencies of the nucleus. Spin-lattice relaxation time measurements for the deuterons were made to try to relate the observed values of T_1 and its temperature and frequency dependence to possible deuteron motions which cause efg fluctuations.

*Despite the term "spin-lattice" relaxation time, processes contributing to T_1 need not be direct interactions between nuclear spins and the types of lattice vibrations usually designated as phonons.

The temperature and frequency dependence of T_1 were measured with the crystalline b axis perpendicular to the applied magnetic field H_0 because the deuteron bonds which are related by the mirror-plane reflection of the monoclinic cell give identical NMR spectra for this relation of the b axis to H_0 . This has the dual advantage of higher line intensity and fewer lines to interfere with the study of the relaxation of a given line. Furthermore, these studies were made where the quadrupolar splitting of the Zeeman levels is zero. ($\theta_b = 8, 61, 150,^\circ$ in Fig. 10.) Besides another gain in intensity of the line under consideration, these locations also have the advantage of being the only locations where it is convenient to alter the populations of the levels and observe return to equilibrium via a single time constant. This is true for any interaction for which $\Delta m = 1$ and $\Delta m = 2$ transitions can occur, and is evident from a consideration of the rate equations for the populations of the levels. Let W_1 and W_2 be the transition probabilities for $\Delta m = 1$ and $\Delta m = 2$ transitions respectively. Let N_1 , N_0 , and N_{-1} be the thermal equilibrium populations of the $m = 1, 0, -1$ levels and let $N_1(t)$, $N_0(t)$, $N_{-1}(t)$ be the populations of these levels at time t . Define the deviation of the i^{th} level from equilibrium at

time t as $n_i = N_i(t) - N_i$. The rate equations for return to thermal equilibrium are:

$$\frac{dn_1}{dt} = -W_1(n_1 - n_0) - W_2(n_1 - n_{-1}) \quad (1a)$$

$$\frac{dn_0}{dt} = -W_1(n_0 - n_1) - W_1(n_0 - n_{-1}) \quad (1b)$$

$$\frac{dn_{-1}}{dt} = -W_1(n_{-1} - n_0) - W_2(n_{-1} - n_1) \quad (1c)$$

$$\text{Now let } n_+ = n_1 - n_0 = N_1(t) - N_1 - N_0(t) + N_0 \quad (2a)$$

$$n_- = n_0 - n_{-1} = N_0(t) - N_0 - N_{-1}(t) + N_{-1} \quad (2b)$$

$$\frac{dn_+}{dt} = -W_2(n_+ + n_-) - W_1(2n_+ - n_-) \quad (3a)$$

$$\frac{dn_-}{dt} = -W_2(n_- + n_+) - W_1(2n_- - n_+) \quad (3b)$$

If $n_+ = n_-$, $\frac{dn_+}{dt} = -2W_2 - W_1$ and relaxation occurs via the single time constant $T_1 = 1/(W_1 + 2W_2)$. If n_+ and n_- are different, the time constants $1/(W_1 + 2W_2)$ and $1/3W_1$ are both present.

If a resonant rf field is applied equally to both $+1 \leftrightarrow 0$ and $0 \leftrightarrow -1$ lines, $n_+ = n_-$ throughout the experiment and relaxation occurs via the time constant $1/(W_1 + 2W_2)$. This is most convenient to do when the two lines coincide.

The temperature and frequency dependence of T_1 (i.e. $1/(2W_2 + W_1)$) for three such locations is plotted in Figs. 13, 14 and 15. In the subsequent discussion, it will be assumed that the relaxation is due entirely to quadrupolar interactions caused by deuteron motions, i.e. it is assumed that there is no significant contribution to deuteron relaxation from the relatively temperature-independent process of spin diffusion to paramagnetic impurities. This mechanism is often dominant⁽³⁹⁾ for nuclei of spin $I = \frac{1}{2}$, for these nuclei have no electric quadrupolar moment, and may become dominant for deuterons⁽⁴⁰⁾ and other nuclei which have quadrupolar moments when the substance is at a low enough temperature that nuclear and molecular motions are negligible. The assumption of negligible spin-diffusion contribution to the relaxation is based on a comparison of the spin-lattice relaxation time of the protons (13%)* present in the samples studied with the spin-lattice relaxation time of the deuterons. This estimate is discussed in more detail in Appendix A. If one calculates the ratio of deuteron T_1 to proton T_1 for a deuteron to proton ratio of 87/13, assuming

* This calculation was determined from the transition temperature using the transition temperature vs concentration curve of Blinc and Vovk.⁽⁴⁾

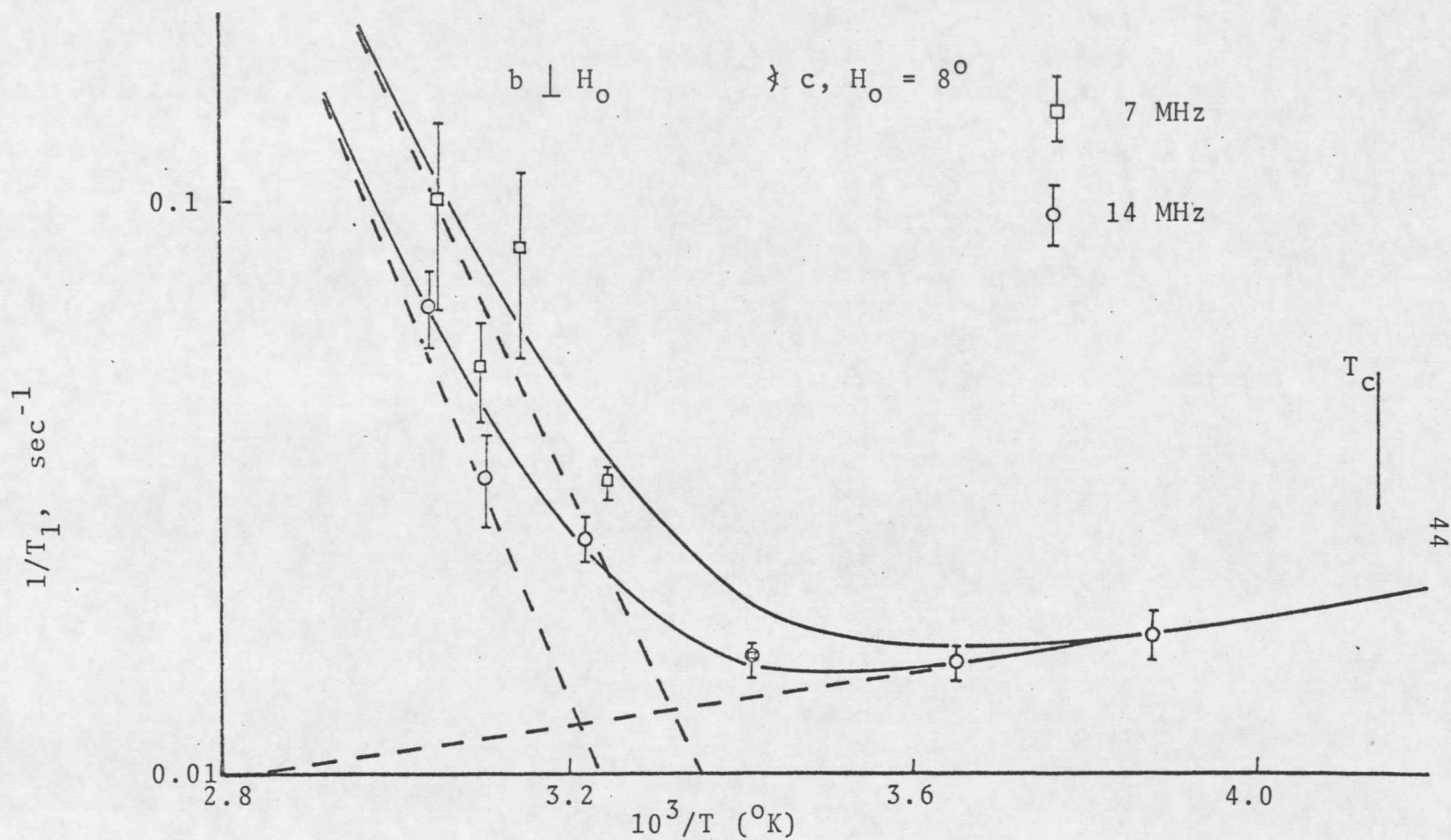


Figure 13: Deuteron T_1 Measurements

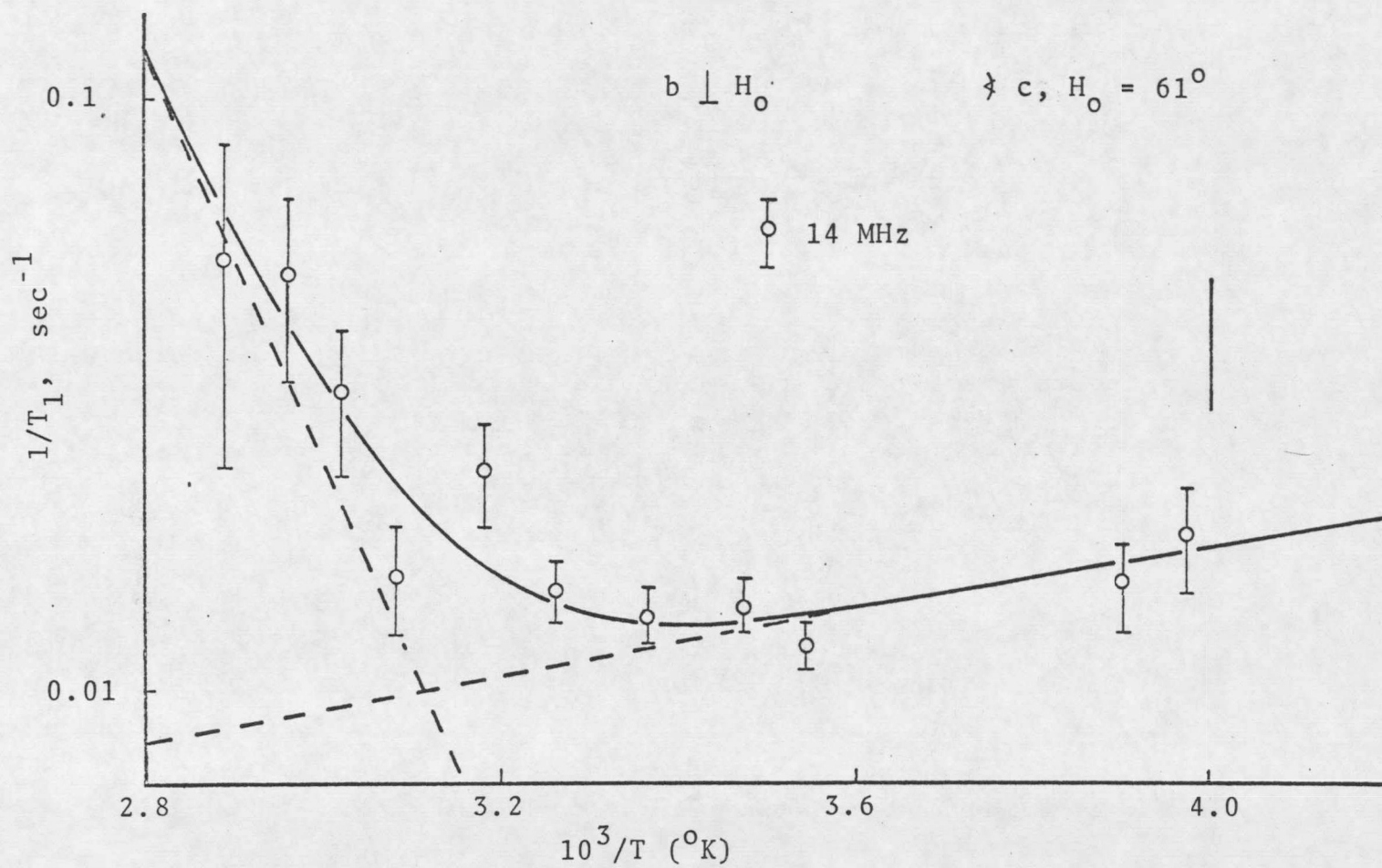


Figure 14: Deuteron T_1 Measurements

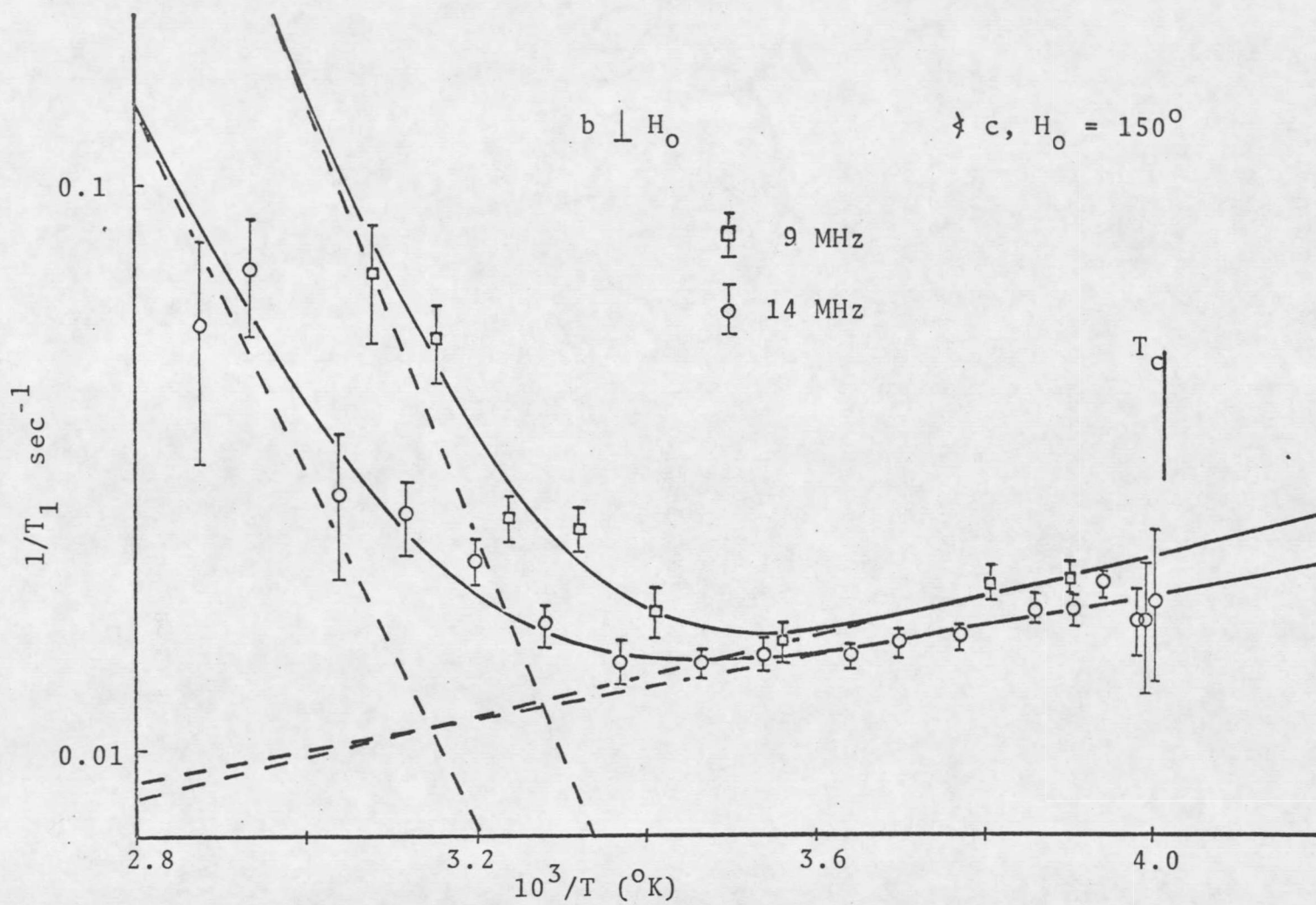


Figure 15: Deuteron T_1 Measurements

that both deuteron and proton relaxation is due entirely to spin diffusion to paramagnetic impurities, one obtains: deuteron T_1 /proton $T_1 = 26$. The measured proton relaxation time was about 150 seconds. Assuming relaxation due entirely to spin diffusion to paramagnetic impurities for both nuclei, the deuteron relaxation time should then be 3900 sec. Thus spin diffusion has negligible effect on the deuteron T_1 values (≈ 60 sec) actually observed. Furthermore, if the proton T_1 of 150 sec is due only partly to spin diffusion to paramagnetic impurities and partly to some other mechanism, a value of proton T_1 greater than 150 sec should be used in computing the spin diffusion contribution to the deuteron T_1 . In such a case, the spin diffusion contribution to the deuteron relaxation would be even less important.

Calculations of W_1 and W_2 for several cases of deuteron motion in various crystals have been made^(40,41,42) and certain general features of these results are useful in initially interpreting the data in Figs. 13, 14 and 15. If one assumes that the probability for a deuteron to jump out of a certain type of location to another type of location is independent of past history, the autocorrelation function for the deuteron motion is exponential, and one gets expressions for W_1 and W_2 of the following form:

$$W_1 = K_1 \frac{\tau_c}{1 + \omega^2 \tau_c^2} \quad (4a)$$

$$W_2 = K_2 \frac{\tau_c}{1 + 4\omega^2 \tau_c^2} \quad (4b)$$

where τ_c is the correlation time for the motion, ω is the $\Delta m = 1$ transition frequency, and the functions K_1 and K_2 contain differences in various efg tensor components, expressed in the laboratory frame, at the several locations between which deuterons move. All orientational dependence of W_1 and W_2 is contained in K_1 and K_2 . If one further assumes that the deuteron motion is a thermally activated process, of frequency $\nu = \nu_0 e^{-E/kT}$, (5)

$$\text{then the correlation time } \tau_c = \tau_0 e^{E/kT} \quad (6)$$

where ν_0 and τ_0 can be related. In two limiting cases,

$$\text{Case I } \omega^2 \tau_c^2 \gg 1, \quad (7)$$

$$\text{Case II } \omega^2 \tau_c^2 \ll 1, \quad (8)$$

T_1 has exponential dependence on temperature.

Case I corresponds to a long correlation time, hence a slow motion, and in this case

$$\frac{1}{T_1} = W_1 + 2W_2 = \frac{K_1 + K_2/2}{\omega^2} \times \frac{1}{\tau_c} = \frac{K_1 + K_2/2}{\omega^2 \tau_0} e^{-E/kT} \quad (9)$$

This case also illustrates frequency dependence which can be observed by making T_1 measurements at various resonant frequencies. Case II corresponds to a short correlation time, hence a fast motion, and in this case

$$\frac{1}{T_1} = W_1 + 2W_2 = (K_1 + 2K_2)e^{E/kT} \quad (10)$$

In Eq. (9), (Case I), as the temperature increases, T_1 decreases. In Eq. (10), (Case II), as the temperature decreases, T_1 decreases. From the temperature and frequency dependence of the T_1 data in Figures 13, 14 and 15, it is therefore evident that from about $1/T = 2.85$ to $1/T_1 = 3.05 \times 10^{-3}/^\circ\text{K}$, (325 to 250 $^\circ\text{K}$) a slow motion, (Case I), dominates the T_1 process. From about 310 $^\circ\text{K}$ to 250 $^\circ\text{K}$, (the transition temperature in the crystals measured), (Case II), a fast motion dominates the T_1 process. The activation energies associated with the two processes were estimated by fitting a function

$$\frac{1}{T_1} = Ae^{-E_1/kT} + Be^{E_2/kT} \quad (11)$$

to each plot. The results are given in Table XI. The lines $Ae^{-E_1/kT}$, $Be^{E_2/kT}$, and the sum of these is sketched in Figs. 13, 14 and 15.

The values of E_1 obtained for the slow process are of the order (roughly 15% smaller) of the activation energies obtained for the electrical conductivity. The uncertainties in the deuteron T_1 measurements are too large and the temperature range is too short to place any significance in the various measurements. The agreement between the two types of experiments is sufficient to conclude that both the electrical conductivity and the deuteron spin-lattice relaxation time are due to some sort of deuteron jumping from one bond to another.

TABLE XI: ACTIVATION ENERGIES
FROM DEUTERON T_1 MEASUREMENTS

Frequency, MHz	Orientation	E_1 , eV	E_2 , eV
7	8°	0.67	
14	8°	0.73	0.046
14	61°	0.65	0.054
9	150°	0.76	0.075
14	150°	0.63	0.053

An exact formal calculation of T_1 for such a bond-jumping process is desirable, and such a calculation can be made using the measured values of the efg tensor discussed in Chapter III. The correlation time remains an undetermined parameter, but, as will be discussed in the next section,

an experimental estimate of this parameter can be made.

The general calculation is outlined in Appendix B. Here we shall outline the calculation of the autocorrelation functions, $G_1(\tau)$ and $G_2(\tau)$ for W_1 and W_2 , assuming equal jump probabilities between all types of bonds*. These autocorrelation functions are

$$G_1(\tau) = (F_2(\tau) F_2^*(t + \tau)), \quad (12a)$$

$$G_2(\tau) = (F_4(\tau) F_4^*(t + \tau)), \quad (12b)$$

$$\text{where } F_2 = V_{-1} = \overline{\phi_{x'z'}} - i\overline{\phi_{y'z'}}, \quad (13a)$$

$$F_4 = V_{-2} = \overline{\phi_{x'x'}} - \overline{\phi_{y'y'}} - 2i\overline{\phi_{x'y'}}, \quad (13b)$$

where ϕ is the electrostatic potential at the deuteron site in a bond and x' , y' and z' are the axes of the laboratory frame, with z' along the applied magnetic field, y' along the axis of rotation (crystalline b axis in this case) and x' perpendicular to the other two in a right-handed sense. The notation $\overline{\phi_{x'z'}}$ means the partial derivative of ϕ with respect to x' and z' . The bars over the terms in brackets of Eq. (12) indicate an ensemble average which is taken by averaging over

*This is not a particularly good assumption but there is no information available to indicate how the probabilities of jumps to different bonds differ from one another.

the initial positions of the deuteron. Although there are only two chemically different types of bonds in the crystal (N and S), these types have different physical orientations, related by the mirror plane of the monoclinic $P 2/m$ group. The tensor components in the crystal and lab frames are different for the different types, so we must consider four types of bonds, with twice as many of each N type as S type. Let F^1, F^2, F^3, F^4 be the appropriate efg components for the N^1, S^1, S^2, N^2 bonds.

TABLE XII: EFG TENSOR COMPONENTS IN CRYSTAL SYSTEM

	$K\phi_{XX}$	$K\phi_{YY}$	$K\phi_{ZZ}$	$K\phi_{XY}$	$K\phi_{XZ}$	$K\phi_{YZ}$
N^1	87.4	-56.8	-30.6	97.8	-90.4	-50.7
S^1	54.4	-99.5	45.1	-19.1	169.8	2.7
S^2	54.4	-99.5	45.1	19.1	-169.8	2.7
N^2	87.4	-56.8	-30.6	-97.8	90.4	-50.7

in units of kHz

The autocorrelation function for equal jump probabilities between all types of bonds is

$$\frac{1}{36} [4(F^1 - F^4)^2 + 2(F^1 - F^2)^2 + 2(F^1 - F^3)^2 + F^2 - F^3)^2 + 2(F^2 - F^4)^2 + 2(F^3 - F^4)^2] e^{-6WT} + \text{const.} \quad (14)$$

This calculation is outlined in Appendix C. The constant contributes nothing to the spectral density so it may be ignored.

We may identify $1/6W$ as the correlation time, (τ_c) , of the jumping motion. After using the result (14) and the values of Table XII one obtains for W_1 and W_2 , assuming $\omega^2 \tau_c^2 \gg 1$,

$$W_1 = \frac{1}{9} \left[\frac{1}{v^2 \tau_c^2} \right] \frac{1}{36} \left[(4.13 - 1.54 \cos 2\theta_X + 2.51 \sin 2\theta_X - 0.0026 \cos 4\theta_X - 0.0221 \sin 4\theta_X) \right] \times 10^{11}, \text{sec}^{-1} \quad (15a)$$

$$W_2 = \frac{1}{36} \left[\frac{1}{v^2 \tau_c^2} \right] \frac{1}{36} \left[(14.29 + 6.43 \cos 2\theta_X - 8.98 \times \sin 2\theta_X + 0.111 \cos 4\theta_X + 0.091 \sin 4\theta_X) \right] \times 10^{11}, \text{sec}^{-1} \quad (15b)$$

Here $v = \omega/2\pi$ is the $\Delta m = 1$ transition frequency of the deuteron. Fig. 16 illustrates the orientational dependence of Eqs. (15a,b). The term in brackets in (15a) is plotted for W_1 and $\frac{1}{2}$ the term in brackets in (15b) is plotted for W_2 so that $W_1 + 2W_2$ may be found at any angle θ_b by adding the values of the two curves in Fig. 16 and multiplying by $10^{11} / 9 \times 36 \times v^2 \tau_c^2$.

The frequency-independence of T_1 in the lower temperature (20°C to -20°C) region and the decrease of T_1 with decreasing temperature indicates that a relatively high-frequency motion is responsible for relaxation in this range. The exponential dependence on temperature suggests a thermally

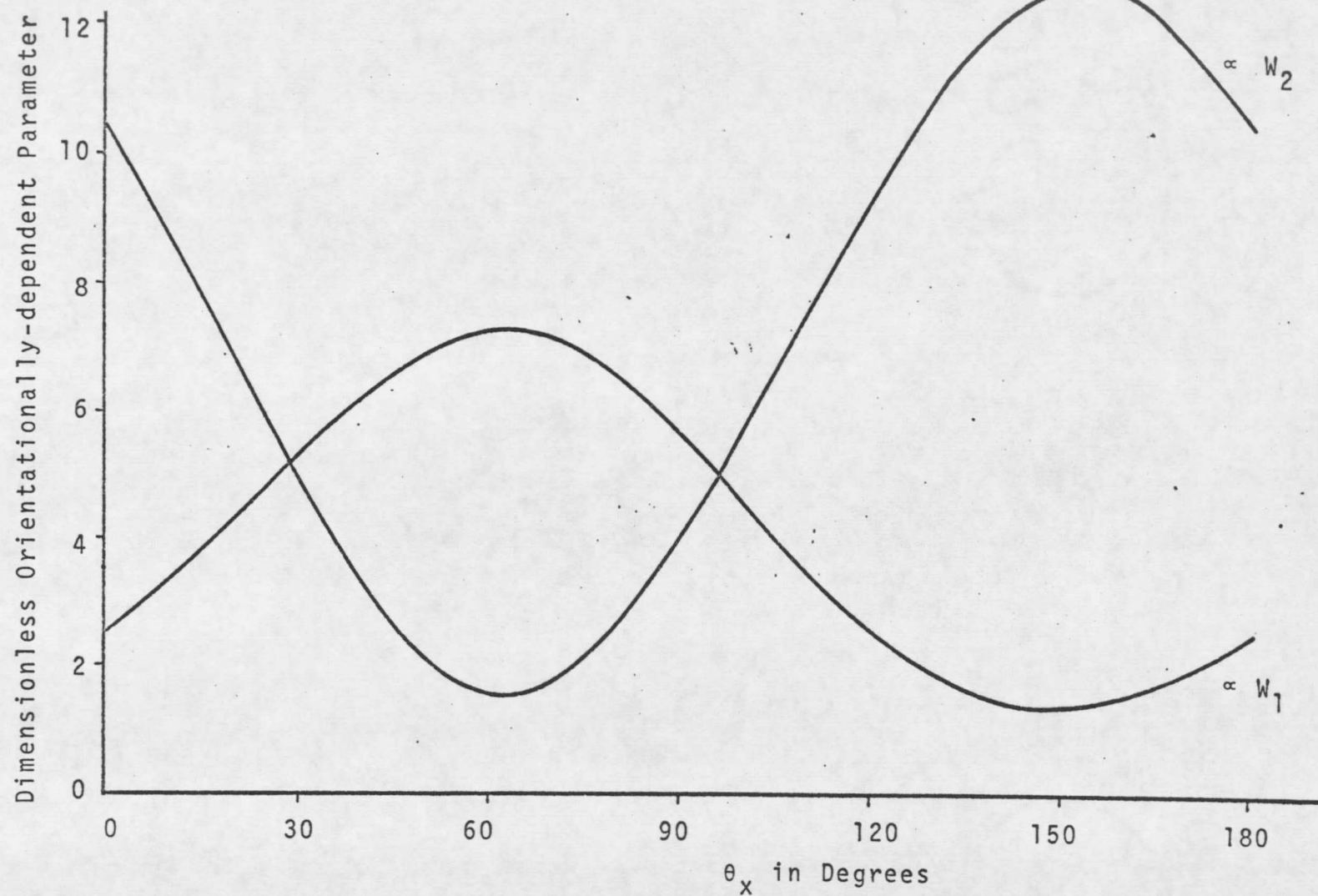


Figure 16: Orientational Dependence of Interbond Jumping Contribution to W_1 and W_2

activated process and from the values of Table XI, the activation energy is about 0.055 eV. Deuteron intrabond motion is a process which could be the cause of the relaxation in this range. However, the deuterons in the S bonds should not be able to relax by such a process if they jump between sites which are equidistant from the center of the bond because the center of the bond is a center of symmetry in the unit cell. All efg tensor components should be the same at sites related by an inversion through this point. Nevertheless, a comparison of Figs. 13, 14 and 15 shows that the temperature dependence of the relaxation of the S bond in Fig. 14 is similar to that of the N bonds in Figs. 13 and 15. The deuterons in S bonds can, of course, relax via intrabond motion if they exchange sites in a time short compared to T_1 for intrabond motion in N bonds. We would therefore expect that, even down to -20°C , the jump time (τ_j^*) of deuterons from N bonds to S

* τ_j is used to represent the mean deuteron interbond jump time between N and S bonds. It should be noted that in Eqs. (4 - 9) τ_c is used in a general sense to represent the correlation time of whatever motion is under consideration. If the jump probabilities between all types of bonds in the cell are the same, as was assumed for the calculation in this section, τ_j is also the appropriate correlation time (τ_c) for Eqs. (15a,b). An extreme example of deuteron interbond motion where τ_j and τ_c would be different is a case where there is interbond jumping between N^1 and N^2 bonds and also between S^1 and S^2 bonds, but no exchange between N and S bonds. In such a case, τ_j is infinite but there is a correlation time τ_{cN} for the N bonds and another τ_{cS} for the S bonds.

bonds is short compared to T_1 at -20°C , ie, $\tau_j < 60 \text{ sec}$.

SECTION III: Deuteron Interbond Jump Time

From the previous discussion, it is evident that a direct measurement of the deuteron interbond jump time (τ_j) would be valuable. This time is the only undetermined parameter in the calculation of the spin-lattice relaxation due to interbond jumping, and it must satisfy an upper limit condition for the observed temperature dependence of T_1 in the 20 to -20°C range in order to be explained by intrabond jumping.

The experimental technique applied measured the jump time (τ_j) between N and S bonds directly. It consisted of a sequence of three 90° pulses applied to the spectrum of one type of bond (the S bonds for Figs. 17, 18, 19) at an orientation at which the quadrupolar splitting of the lines was zero. The following discussion applies to making the measurement where the S bond spectrum is merged, such as was done for the b axis rotation with $\theta_b = 61^\circ$. It also assumes that the jump time is much shorter than T_1 . The effect of the various pulses on the populations is given in Fig. 17. The first 90° pulse reduces the population difference of the S bonds to zero. They recover to $N = (2/3)N_0$ and $S = (1/3)N_0$ as the deuterons exchange sites. The second pulse is applied at a

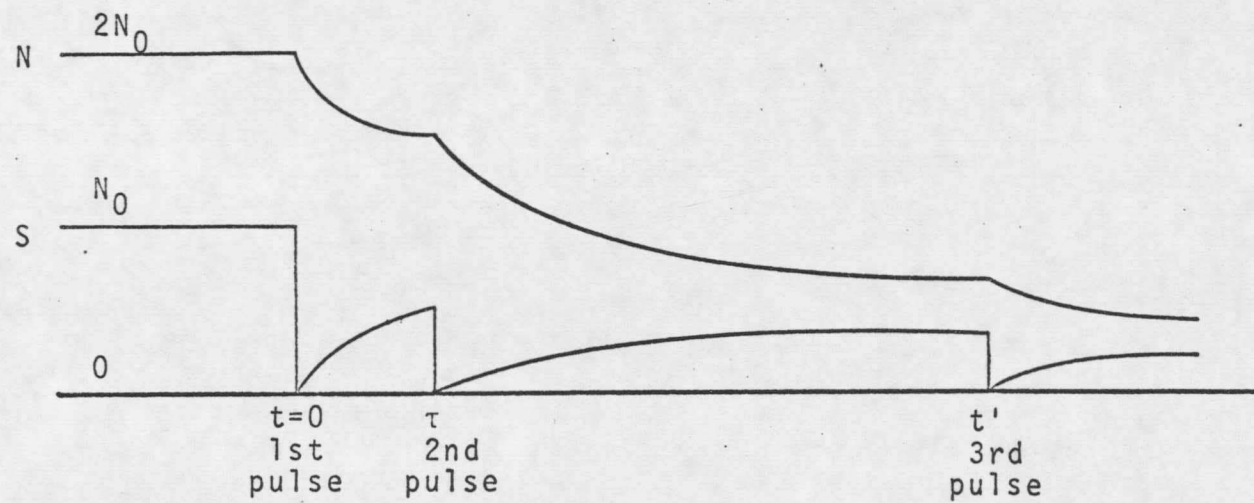


Figure 17: Effect of 3 90° Pulses
on Populations

time τ of the order of τ_j . The response after this pulse, given by

$$V_2 = (2/3)V_0(1 - e^{-\tau/\tau_j}), \quad (16)$$

is recorded and compared to the response after the third pulse

$$V_3 = (2/9)V_0(2 + e^{-\tau/\tau_j}). \quad (17)$$

Here V_0 is the response to the first pulse. The third pulse is applied at a time t' which obeys $\tau_j \ll t' \ll T_1$. The response to pulse 3 is then proportional to $1/3$ the population difference of the N bonds when the second pulse is applied. In the limit $T_1 \gg \tau \gg \tau_j$, $V_3 = (4/9)V_0$. The spacing between the first and second pulses, (τ) , is varied and the ratio V_2/V_3 is recorded for each τ . At $V_2/V_3 = 1$, $\tau/\tau_j = 1.39$. By calculating τ_j from the point where $V_2/V_3 = 1$, non-linearities in the receiver do not introduce errors into the measured value of τ_j . Fig. 18 shows a plot of V_2/V_3 vs τ for a measurement on the S bonds at 28°C. The solid line shows the theoretical values of V_2/V_3 for $\tau_j = 48$ ms.

Such a jump time measurements were made as a function of temperature from 50°C to -15°C. These, illustrated in Fig. 19, are plotted as $\log 1/\tau_j T$ vs $1/T$ because the jump time is expected to have temperature dependence

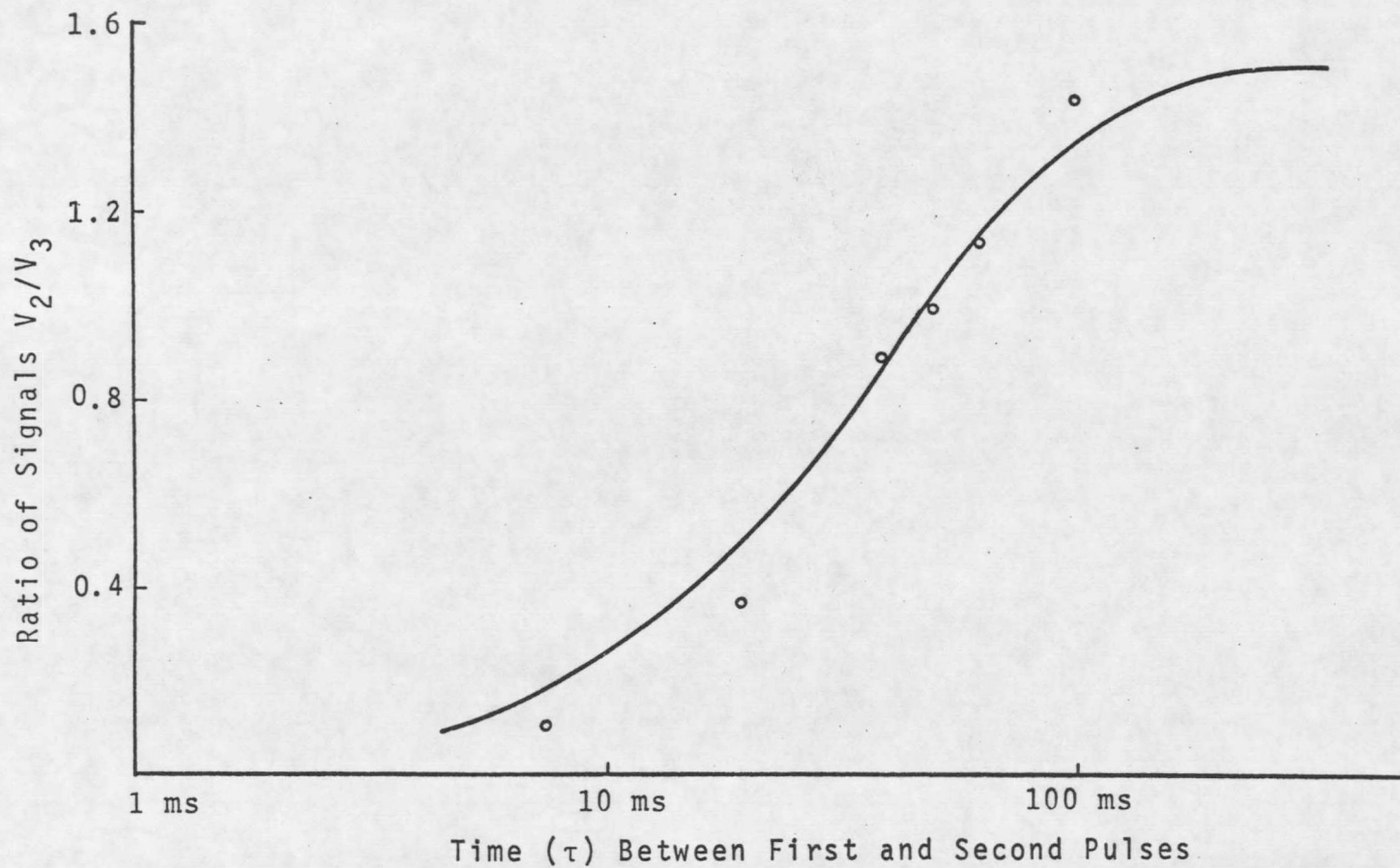


Figure 18: Example of Jump Time Measurement Data

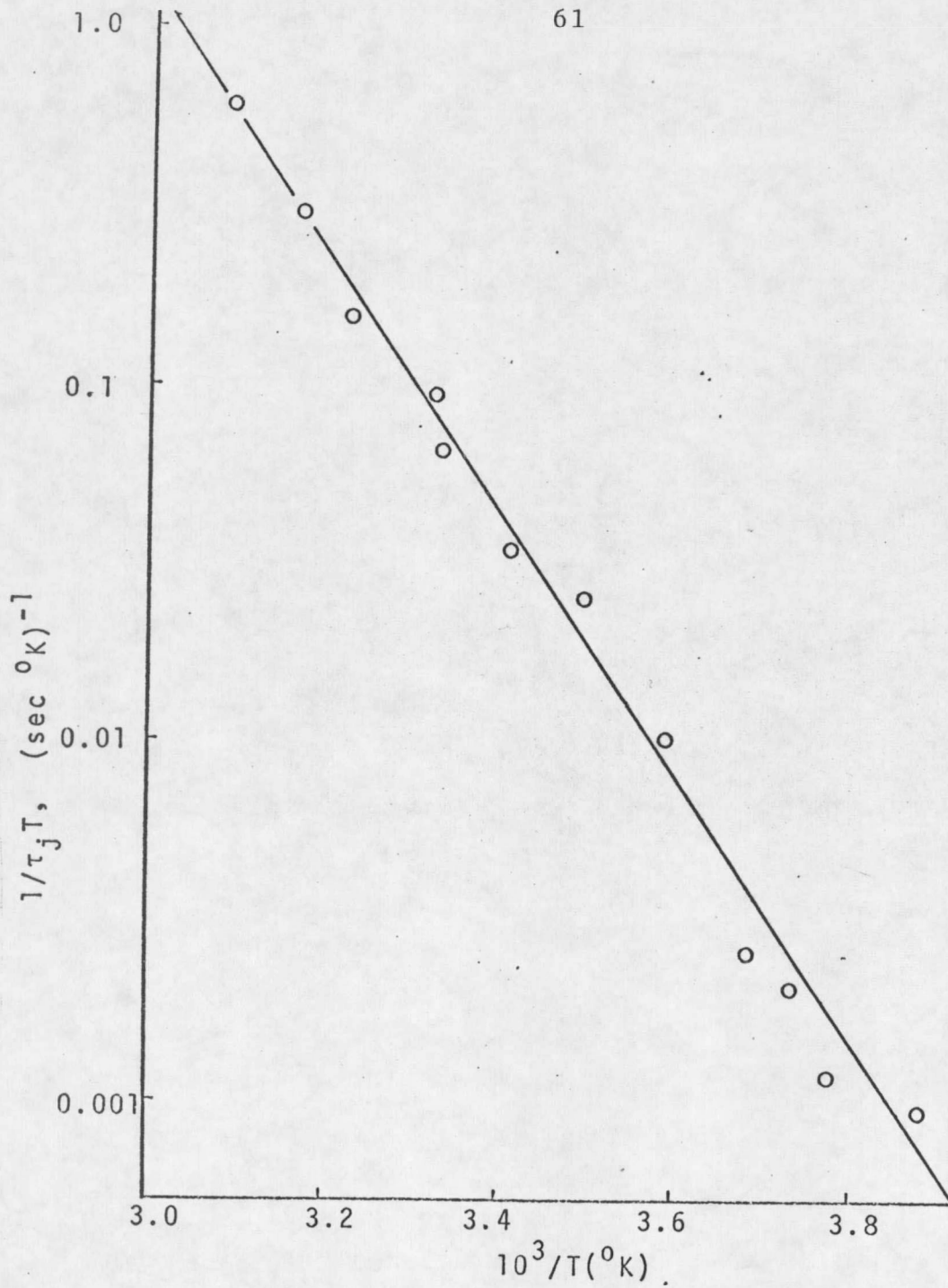


Figure 19: Temperature Dependence
of Deuteron Jump Time

$$\tau_j = \tau_{j0} e^{E/kT}, \quad (18)$$

where τ_{j0} is assumed to vary as h/kT . From Fig. 19, a value of $E = 0.73$ eV is obtained from the slope of the curve and, from the value of τ_j at 303°K , a value of 2.3×10^{-14} sec is obtained for τ_{j0} at this temperature. The accuracy of the jump time measurements is difficult to estimate. By calculating τ_j from the time at which the responses to the second and third pulses are observed to be equal, errors due to non-linearity in the receiver are circumvented. The points plotted in Fig. 19 were averages of four to six individual pulse sequences for each value of τ . Uncertainties in where V_2/V_3 equaled one varied from 5 to 25% depending on the measurement. Since τ_j changed by three orders of magnitude in the temperature range over which it was measured, the deuteron interbond jumping activation energy obtained from these measurements is estimated to be accurate to at least 10%. A comparison with Tables VIII and IX indicate that this value agrees well with the values of the deuteron interbond activation energy obtained from conductivity (0.74 - 0.82 eV) and that obtained from deuteron T_1 measurements (0.63 - 0.76 eV).

The results of Fig. 19 may now be used together with Eqs. (15a,b) to calculate the interbond jump contribution to deuteron T_1 . The T_1 measurements in Figs. 13 - 15 were taken

at $\theta_X = 73^\circ$, 126° and 35° respectively. Assuming a correlation time τ_c of 5.6×10^{-3} sec (see Fig. 19) at 50°C , values of T_1 of 396, 284 and 362 sec, are obtained for a Larmor frequency of 14 MHz. As was previously pointed out, the calculation leading to Eqs. (15a,b) assumes equal jump probability to all bonds in a unit cell, which is probably incorrect. The disagreement between data and the calculation certainly indicates that something is incorrect. A correction of the calculation would most likely involve lower probability of jumping to some bonds. This would leave the terms of the differences of efg tensor components about the same in the numerator of Eqs. (15) but would increase the fraction $1/36$ in front of the autocorrelation function (Eq. 14). Unfortunately, the blatant disagreement here between the model and the experimental results cannot be blamed entirely on the model. The uncertainty in the experimental values is large and the error in the estimate of the interbond contribution to the T_1 data could be off by as much as 50%.

Extrapolating Fig. 19 to the melting point of the crystal (111°C or $1/T = 2.6 \times 10^{-3}/^\circ\text{K}$), τ_j becomes less than 100 sec. As the jump time goes from greater than to less than the inverse of the quadrupolar splitting frequency (~ 100 kHz), one can expect the separate spectra to broaden, dis-

appear, and eventually re-emerge as a single spectrum split by the average of the efg tensors of the sites among which the deuterons exchange. Indirect evidence that the deuteron jump time actually approaches 10^{-5} sec before melting was obtained by observation of the onset of line-broadening at 86°C . The crystal melts before the two spectra reappear as an averaged one, however, so this entire process cannot be observed.

At the low temperature end of Fig. 19, at -23°C ($10^3/T = 4.0$), τ_c is 17 sec, which is less than the T_1 measured at the lowest temperature of the paraelectric phase. This is enough smaller than T_1 that both S and N spectra show similar intrabond relaxation. If the phase transition were 10° lower, τ_j would be long enough that T_1 for the S bond deuterons would approach τ_j . This effect should be observable in a crystal of lower deuteron concentration having a lower transition temperature.

SECTION IV: Sodium Relaxation Time

Blinc and coworkers have made some temperature-dependent measurements of the deuteron⁽²⁹⁾ and sodium⁽⁴³⁾ nuclei in DSTSe with the comment that, because of their similar temperature dependences, the relaxation times of these two nuclei must be due to the same motions. To further investigate this possibility, temperature, frequency, and orientation dependent T_1 measurements of Na^{23} nuclei were made in DSTSe.

The properties of the crystals used in these measurements are summarized in Table XIII. Crystals 9a and 9b were halves of the same single crystal.

TABLE XIII: CRYSTALS USED FOR SODIUM T_1 MEASUREMENTS

Crystal No.	T_c	%D	Data Illustrated of Figure					
			20	21	22	23	24	26
7	-33°C	79	○					
9a	-36°C	74	△		○		○	□
9b	-36°C	74	□	○ □		○	□	○

The T_1 measurements above T_c are plotted in Fig. 18.

These measurements were taken using a $90^\circ - \tau - 90^\circ$ pulse sequence applied to the central ($\frac{1}{2} \leftrightarrow -\frac{1}{2}$) transition of Na^{23} . Relaxation via an electric quadrupolar interaction does not occur directly between these two levels.

Consideration of the rate equations for the populations of the four levels ($\pm 3/2$, $\pm 1/2$) leads to the result that for saturation of the $\frac{1}{2} \leftrightarrow -\frac{1}{2}$ line, subsequent relaxation occurs via two time constants,⁽⁴⁴⁾ $1/2W_1$ and $1/2W_2$, where W_1 is the transition rate for $\Delta m = 1$ transitions between the $3/2, 1/2$ and $-1/2, -3/2$ levels and W_2 is the transition rate for $\Delta m = 2$ transitions between the $3/2, -1/2$ and $1/2, -3/2$ levels. The data did not convincingly display two time constants, probably because the two time constants have about the same value, or because either W_1 or W_2 is negligible. As a result, the raw data was fitted in each case to a single time constant, referred to in Figs. 20-24 as T_1 .

The temperature and frequency dependence of T_1 in Fig. 20 does resemble that of the deuteron T_1 measurements in Figs. 13-15. From about 25°C ($1/T = 3.36 \times 10^{-3}/^\circ\text{K}$) on up in temperature the 8 MHz values of T_1 are shorter than those taken at 14 MHz. From 25°C down to T_c , the values of T_1 are about the same for 8 and 14 MHz.

Figs. 22 and 23 illustrate an analysis assuming that the T_1 data is made up of a high-frequency motion contribution which dominates below 25°C and a low-frequency motion contribution which dominates above 25°C . Although the 14 MHz data of Fig. 22 and the 8 MHz data of Fig. 23 were taken

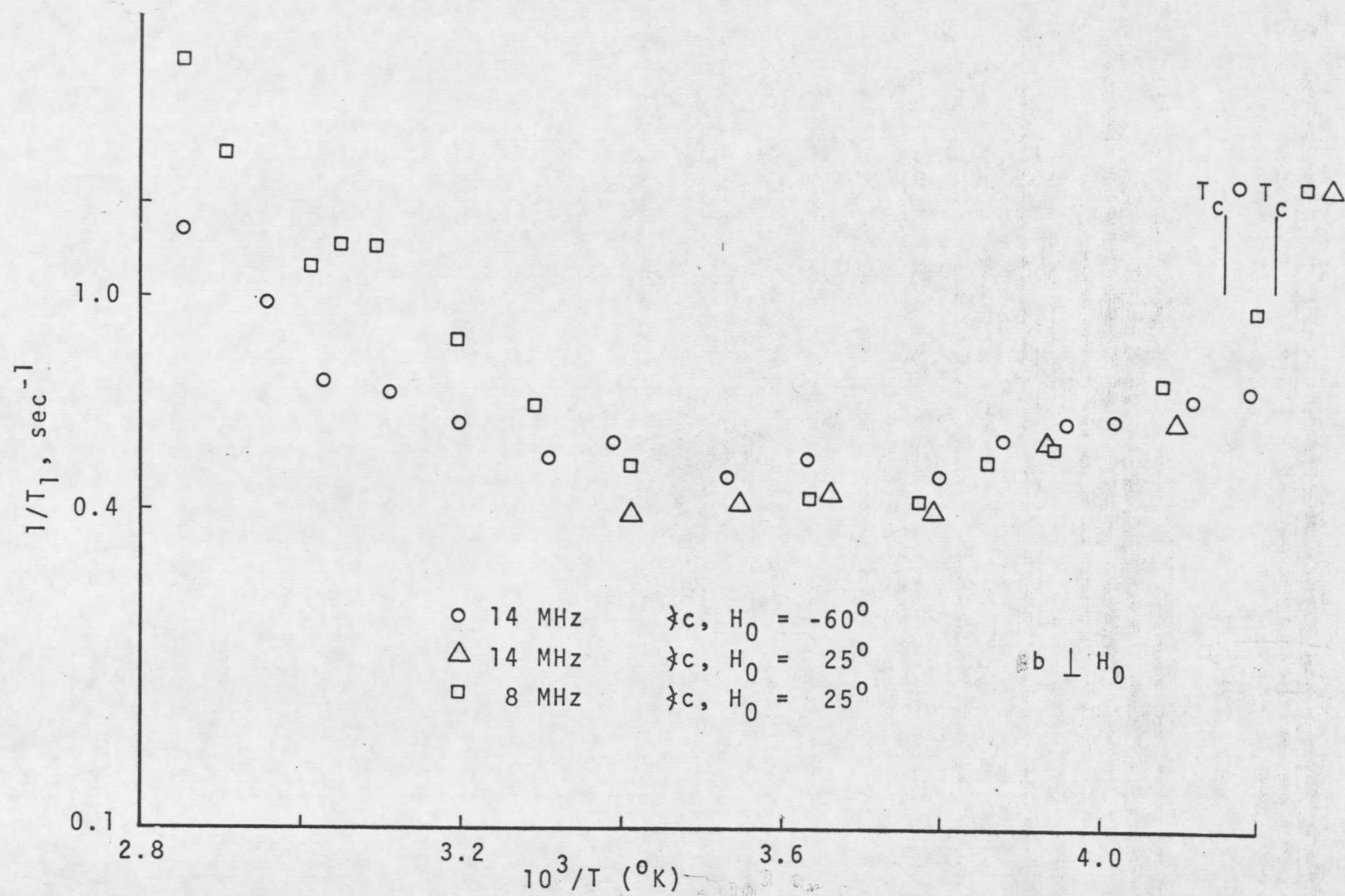


Figure 20: Na^{23} T_1 Measurements Above T_c

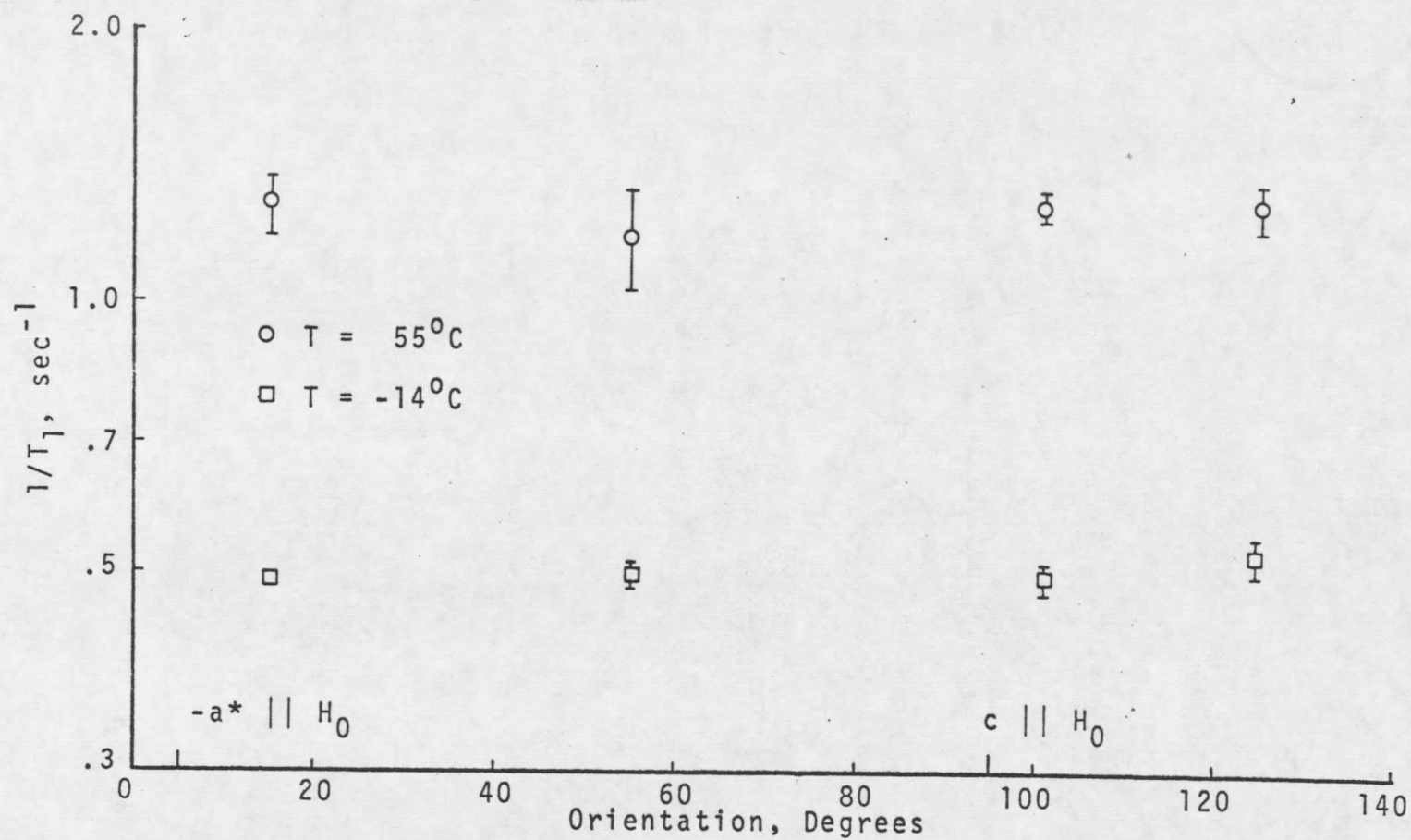


Figure 21: Orientational Dependence of $\text{Na}^{23} T_1$ at 8 MHz

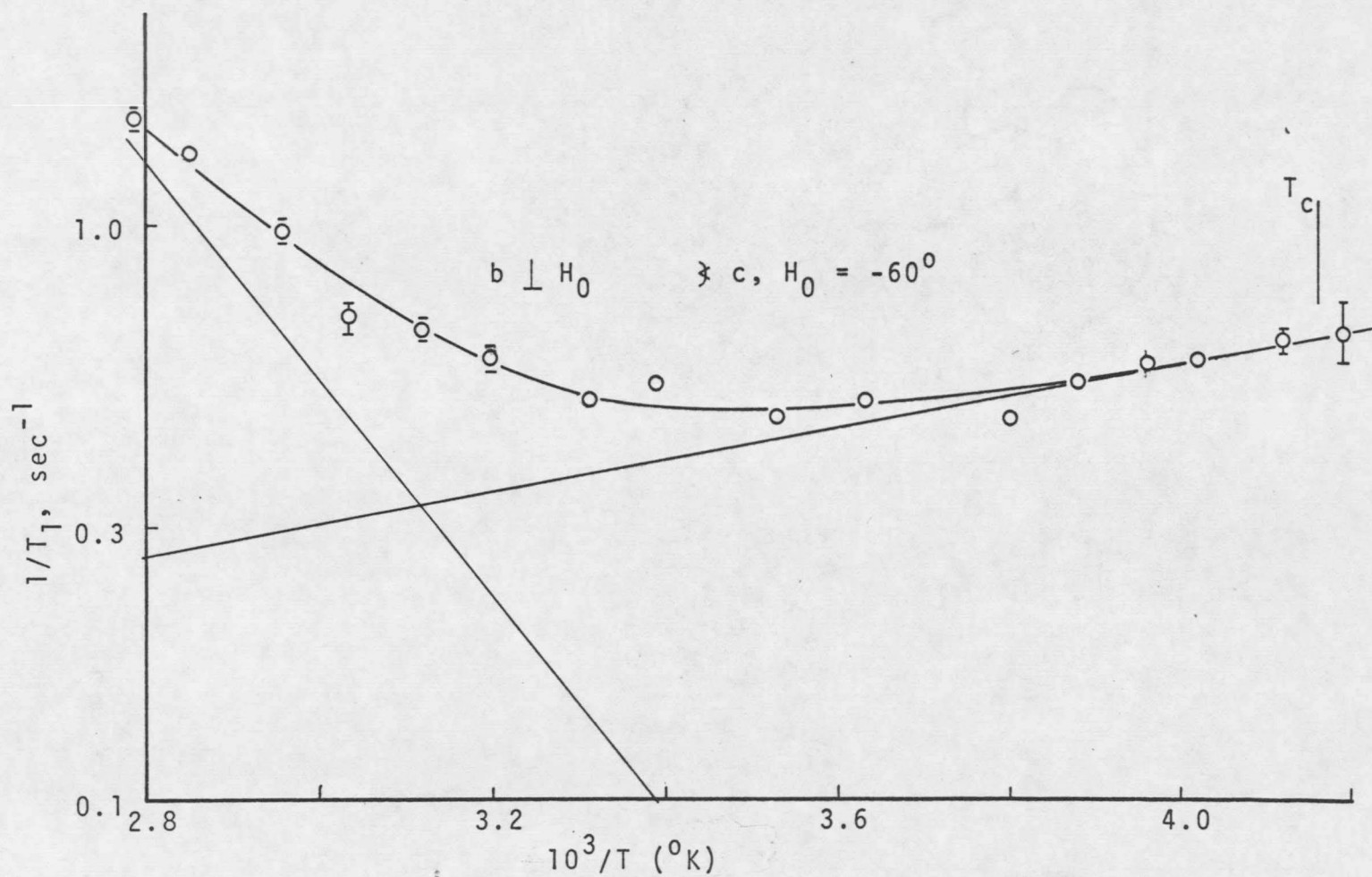


Figure 22: $\text{Na}^{23} T_1$ Measurements at 14 MHz

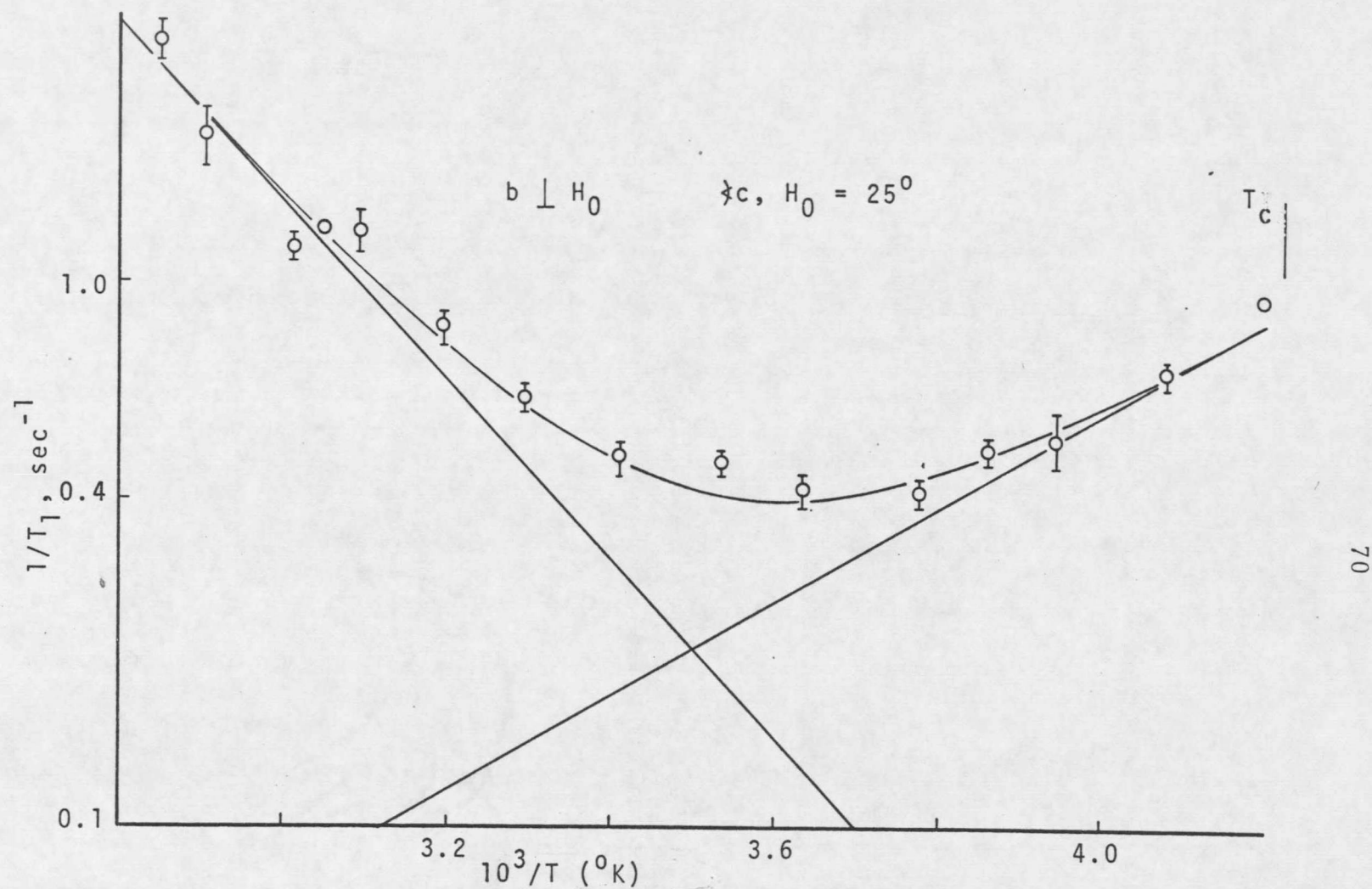


Figure 23: $\text{Na}^{23} T_1$ Measurements at 8 MHz

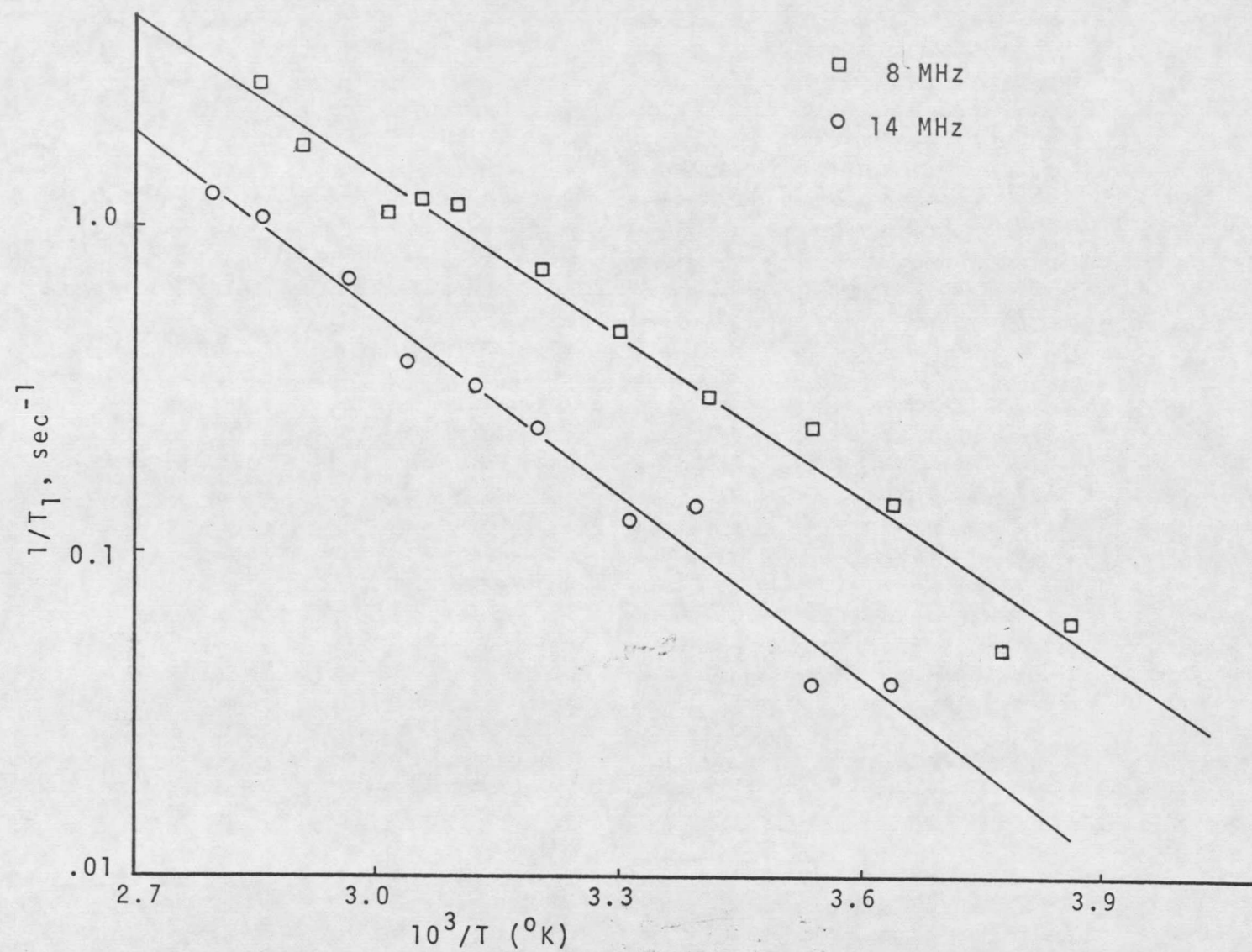


Figure 24: High Temperature Mechanism Contribution to $1/T_1$

at different orientations, no adjustment of the magnitudes of either portion of either curve was made to account for orientational dependence. The orientationally dependent data taken at 8 MHz and illustrated in Fig. 21 shows that neither mechanism is significantly orientationally dependent. The resulting curves in Figs. 22 and 23 are described by Eq. (11) with the activation energies summarized in Table XIV.

TABLE XIV: ACTIVATION ENERGIES
FROM Na^{23} T_1 MEASUREMENTS

Frequency	E_1 , eV	E_2 , eV
8 MHz	0.32	0.17
14 MHz	0.37	0.05

Fig. 24 illustrates the high-temperature contribution alone. The points were obtained by subtracting the line $\text{Be}^{E_2/kT}$ from each T_1 measurement. The solid lines are the high temperature contribution, $\text{Ae}^{-E_1/kT}$, fit to each set of points. From Eq. (7), the lines should be in the ratio $(14 \text{ MHz})^2 / (8 \text{ MHz})^2 = 3.06$.

From these results it is fairly convincing that the dominant contribution to the relaxation times of Na^{23} in the 75°C to 30°C range is of the slow-motion form described by Eq. (7) and referred to as Case I on page 49. From Fig. 20, it also seems that from 0°C to -30°C , the dominant

mechanism is of the form referred to as Case II, although the activation energies for the 8MHz and 14 MHz measurements in this region are quite different. This disparity is partly the result of this mechanism dominating, especially in the 8 MHz case, only over a short temperature range. It is difficult to get an accurate measurement of such a small energy over such a short temperature range.

The disturbing fact about these results is that the energies E_1 are only about $\frac{1}{2}$ the deuteron interbond jump energies obtained from conductivity, deuteron T_1 measurements and direct measurements of the deuteron jump time. Because of this difference, it is pertinent to investigate the possibility that the deuteron conductivity is dependent on two activation energies, one for carrier creation (E_n) and one for carrier mobility (E_m). The conductivity is then of the form

$$\sigma = \sigma_0 \exp - (\frac{1}{2}E_n + E_m) / kT. \quad (19)$$

The contribution to sodium relaxation of interest is the fluctuation of the efg tensor at the sodium site due to the presence of an extra deuteron in, or the absence of any deuteron in, a nearby hydrogen bond. The correlation time associated with this process may be very short (shorter

than the Larmor period of the Na^{23} nucleus) if such defects are fairly mobile, or longer than the Larmor period if such defects have a tendency to get trapped in particular localities for longer periods of time. The frequency dependence of T_1 would be different for these two cases and the part of the total conductivity energy which each depends on would be different as well.

Let τ_m be the mean lifetime of a defect at a particular bond, and τ_n be the mean time between the occurrence of defects near a Na^{23} site. Assume $\tau_m \ll \tau_n$. Then τ_n and the conductivity are related by*

$$\sigma = e^2 / 6a_o kT \tau_n, \quad (20)$$

where e is the electronic charge, a_o is the mean distance between hydrogen bonds, and kT is the thermal energy. The factor 6 comes from assuming 6 nearest bonds to a deuteron site. We may assume τ_m to be of the form

$$\tau_m = T_0 \exp(E_m/kT). \quad (21)$$

Then the autocorrelation function for defect motion is of the form

* This calculation is done in more detail in Appendix D.

$$G(\tau) \propto \frac{\tau_m}{\tau_n} \exp(-\tau/\tau_m). \quad (22)$$

The resulting spectral density is of the form

$$J(\omega) \propto \frac{2\tau_m^2}{\tau_n} \frac{1}{1 + \omega^2\tau_m^2}. \quad (23)$$

If it is assumed that $\omega^2\tau_m^2 \ll 1$, then

$$J(\omega) \propto \frac{2\tau_m^2}{\tau_n} = 2 \exp(-(E_n - 2E_m)/2kT) \quad (24)$$

In the other extreme, if the trapping is sufficiently long, $\omega^2\tau_m^2$ may be much greater than 1 and

$$J(\omega) \propto \frac{2}{\omega^2\tau_n} \propto \frac{\sigma}{\omega^2} \quad (25)$$

Neither of these cases agrees with the data as analyzed in Figs. 22 and 23. Eq. (24) leads to a result for T_1 which is independent of frequency. This is inapplicable to the results, particularly as presented in Fig. 24. Eq. (25) has the proper frequency dependence but indicates that the activation energy for the T_1 process should be the same as the total activation energy for conductivity.

This leaves two possibilities for the high temperature (75°C to 30°C) contribution to the $\text{Na}^{23} T_1$: either this relaxation is due to some slow motion other than deuteron interbond jumping and with lower (≈ 0.35 eV) activation

energy, or a third relaxation mechanism is also present in some or all of the 75°C to -30°C range which must be subtracted from the raw T_1 data to obtain the correct contribution to the mechanism which dominates at the high temperature end of this region.

A numerical estimate of the ratio $1/T_1$ sodium to $1/T_1$ deuterium may be made for the deuteron interbond jumping case using Eqs. (9,20,25). At 300°K, $1/T_1$ sodium equals $400 \times 1/T_1$ deuterium, using the appropriate quadrupolar moments, an antishielding factor of 5.5 for Na^{23} , and assuming equal field gradient changes for the two nuclei. From Figs. 13 and 22, the experimental ratio at 300°K is $.13\text{sec}^{-1}/.004\text{sec}^{-1} = 35$. This ratio was also calculated for deuteron intrabond motion, assuming antishielding factors of 5.5 for Na^{23} and 1 for H^2 . A ratio of squares of efg component changes for $\text{Na}^{23}/\text{H}^2$ was estimated to be 0.014 from point charge models. In this case, $1/T_1$ sodium equals $555 \times 1/T_1$ deuterium, compared to experimental values of $0.44\text{sec}^{-1}/0.014\text{sec}^{-1} = 31$ at 278°K from Figs. 13 and 22. While calculated and experimental ratios differ by more than an order of magnitude in each case, the efg changes, which enter the ratio in the second power for each type of nucleus, are not accurately estimated, and the correct antishielding factor for a deuteron in a hydrogen bond is not known.

CHAPTER V: SPIN-LATTICE RELAXATION TIME MEASUREMENTS BELOW T_c

Below the transition, the spectrum from deuteron S bonds splits into two spectra and the spectrum from deuteron N bonds splits into four spectra for the b axis rotation. These are illustrated in Fig. 10. Wherever the splitting of one spectrum goes to zero, another spectrum is split slightly and the three lines usually cannot be resolved sufficiently for a measurement of T_1 . At two locations, $\theta_b = 4^\circ$ and $\theta_b = 140^\circ$, the lines are sufficiently resolved that measurements can be made. Fig. 25 illustrates T_1 measurements made on two different crystals at several frequencies in the temperature range from T_c (about 240°K) to liquid air temperature. These measurements were all taken at $\theta_b = 140^\circ$. A few measurements were taken at either end of this temperature range at the $\theta_b = 4^\circ$ location. These agreed reasonably well with those plotted in Fig. 25 but were less precise because the signal/noise is poorer at this orientation.

Below the transition, the sodium spectrum, including the central ($\frac{1}{2} \leftrightarrow -\frac{1}{2}$) line splits into two spectra. The central lines are shifted by the quadrupolar interaction in second order. At two location, $\theta_b = 48^\circ$ and $\theta_b = -25^\circ$, (30)

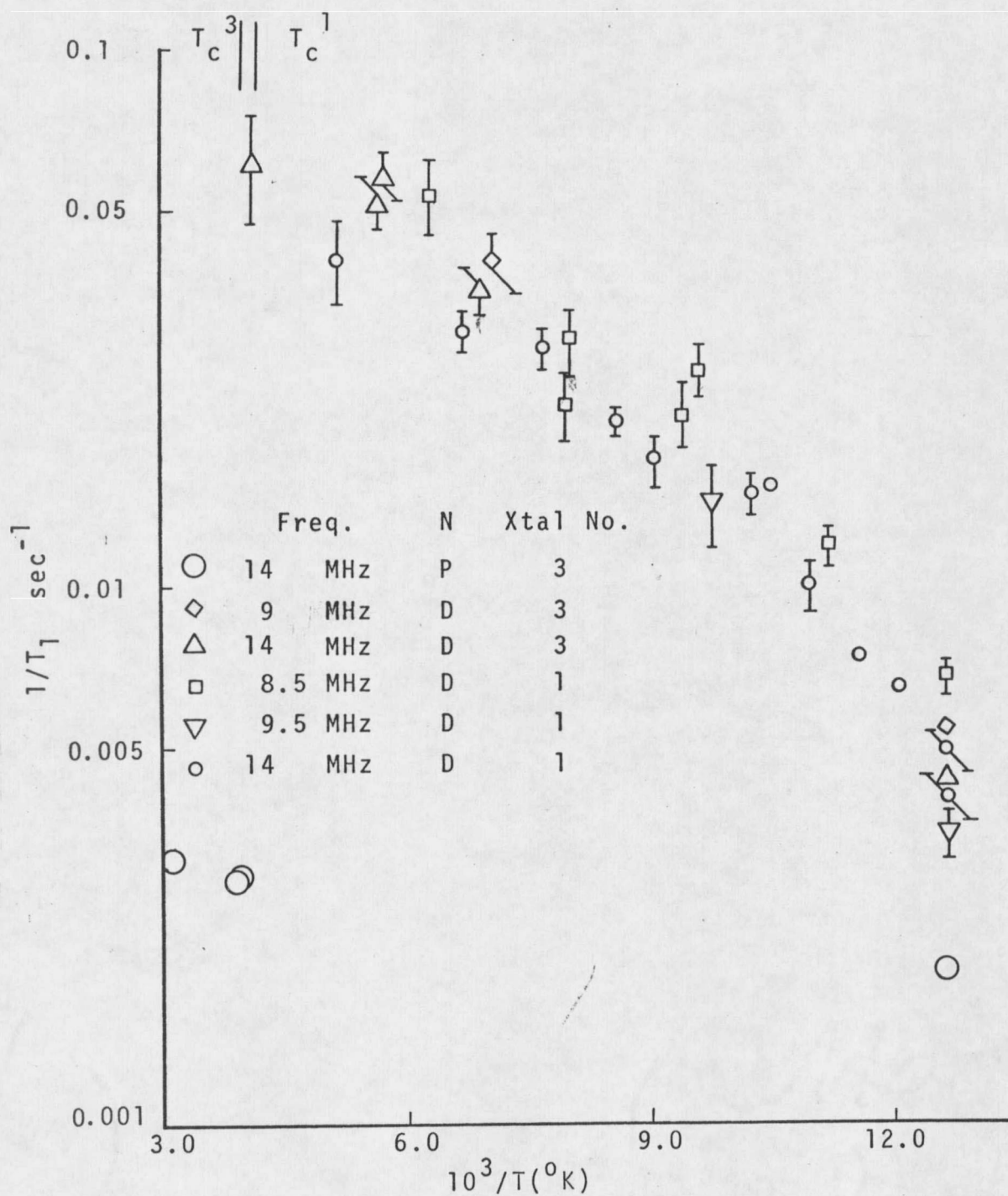


Figure 25: Deuteron T_1 Below T_c and Proton T_1

these shifts are equal. T_1 measurements of this combined central line were made using a $90^\circ - \tau - 90^\circ$ pulse sequence. These measurements, whose results are illustrated in Fig. 26, cover a temperature range from T_c (238°K) to about 125°K and were made at 8 MHz and at 14 MHz.

Several features of the T_1 measurements for these two nuclei are similar. In each case, in the region where T is just less than T_c , T_1 shortens. From about 235°K to 185°K , T_1 is approximately constant. Below 185°K , T_1 gets steadily longer, in such a manner that the plot of $\ln 1/T_1$ vs $1/T$ is a straight line. To a rough approximation, an energy of 0.026 eV can be associated with this increase of T_1 . The relaxation times of both nuclei are frequency independent below T_c . Because the relaxation times for these two nuclei (H^2 and Na^{23}) have these features in common in this temperature range, it is likely that their relaxation is due to the same motion. Since the values of T_1 get shorter rather abruptly immediately below the transition, it must be assumed that either a change in the effectiveness of the dominant relaxation mechanism occurs, or else a new dominant mechanism results because of the occurrence of the ferroelectric phase.

In this work, no mechanism has been proposed which

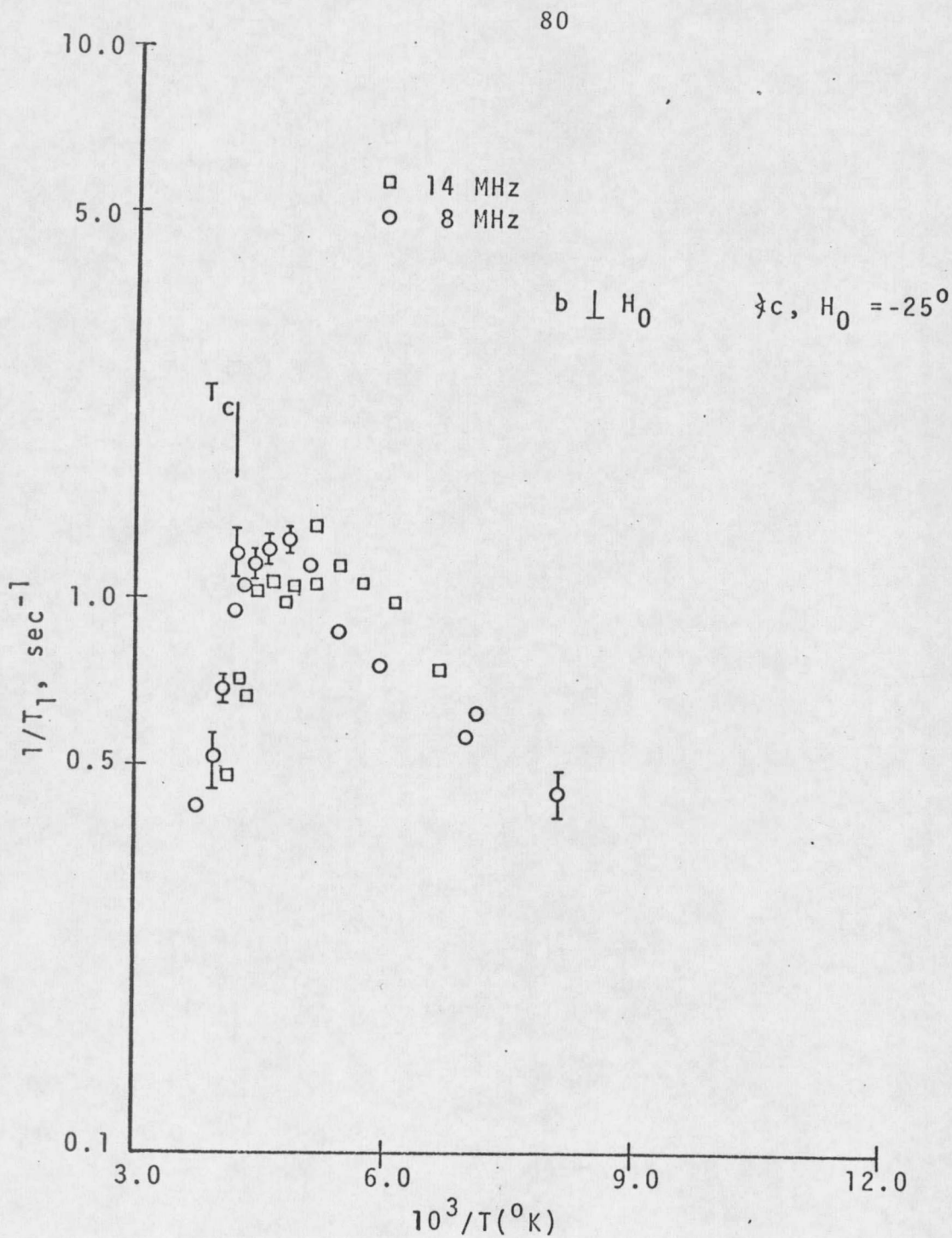


Figure 26: $\text{Na}^{23} T_1$ Below T_c

quantitatively or even qualitatively explains all of these features of the deuteron and sodium T_1 measurements below T_c . However, it is worthwhile to consider the behavior of T_1 which would result from some of the motions which might be expected to accompany the onset of the ferroelectric state.

It should be noted that the general features of the random quadrupolar fluctuation treatment discussed on page 48 is not applicable here. From conditions (7) and (8), when T_1 increases as the temperature is lowered, T_1 is also proportional to the square of the frequency. The fact that this treatment is inadequate means, for example, that it cannot be assumed that the onset of the ferroelectric transition simply resulted in a discontinuous lengthening of the deuteron intrabond jump correlation time from a value where $\omega^2 \tau_c^2 \ll 1$ to a value where $\omega^2 \tau_c^2 \approx 1$. If such were the case, T_1 would attain its shortest value somewhat below T_c and begin to increase with decreasing temperature, as both H^2 and $Na^{23} T_1$'s do, but T_1 would also be frequency dependent, which the H^2 and $Na^{23} T_1$'s are not.

As discussed in Chapter III, the deuteron NMR spectra indicate that in the ferroelectric state, the deuterons are located at the preferred ends of bonds. This ordering could

be expected to have an effect of the T_1 of the deuterons similar to the effect which was observed by Schmidt in KD_2PO_4 .^(40,46) With the onset of polarization, the spectral density becomes of the form

$$J(\omega) \propto \frac{1}{4}(1 - p^2) \frac{2\tau_c}{1 + \omega^2 \tau_c^2} \quad (26)^{26}$$

where p is the fractional polarization and ω and τ_c are used as they were in Chapter IV. As the polarization increases with decreasing temperature, the spectral density decreases and intrabond motion soon contributes negligibly to T_1 . Fig. 27 illustrates deuteron T_1 data in the vicinity of T_c together with a line indicating the effect of the suppression of the spectral density by the polarization factor. The fractional polarization was calculated from the data of Shuvalov.⁽⁶⁾ Clearly, the deuteron T_1 data is not determined by such a mechanism.

In contrast to the T_1 behavior observed in a crystal such as KD_2PO_4 whose transition is primarily of the order-disorder type, there have been several observations^(44,47) of shortening of T_1 in the vicinity of the transition due to large fluctuations in an optical mode which goes to low energy in the region of the transition. In the case of sodium nitrite⁽⁴⁴⁾ the relaxation of the Na^{23} nuclei was

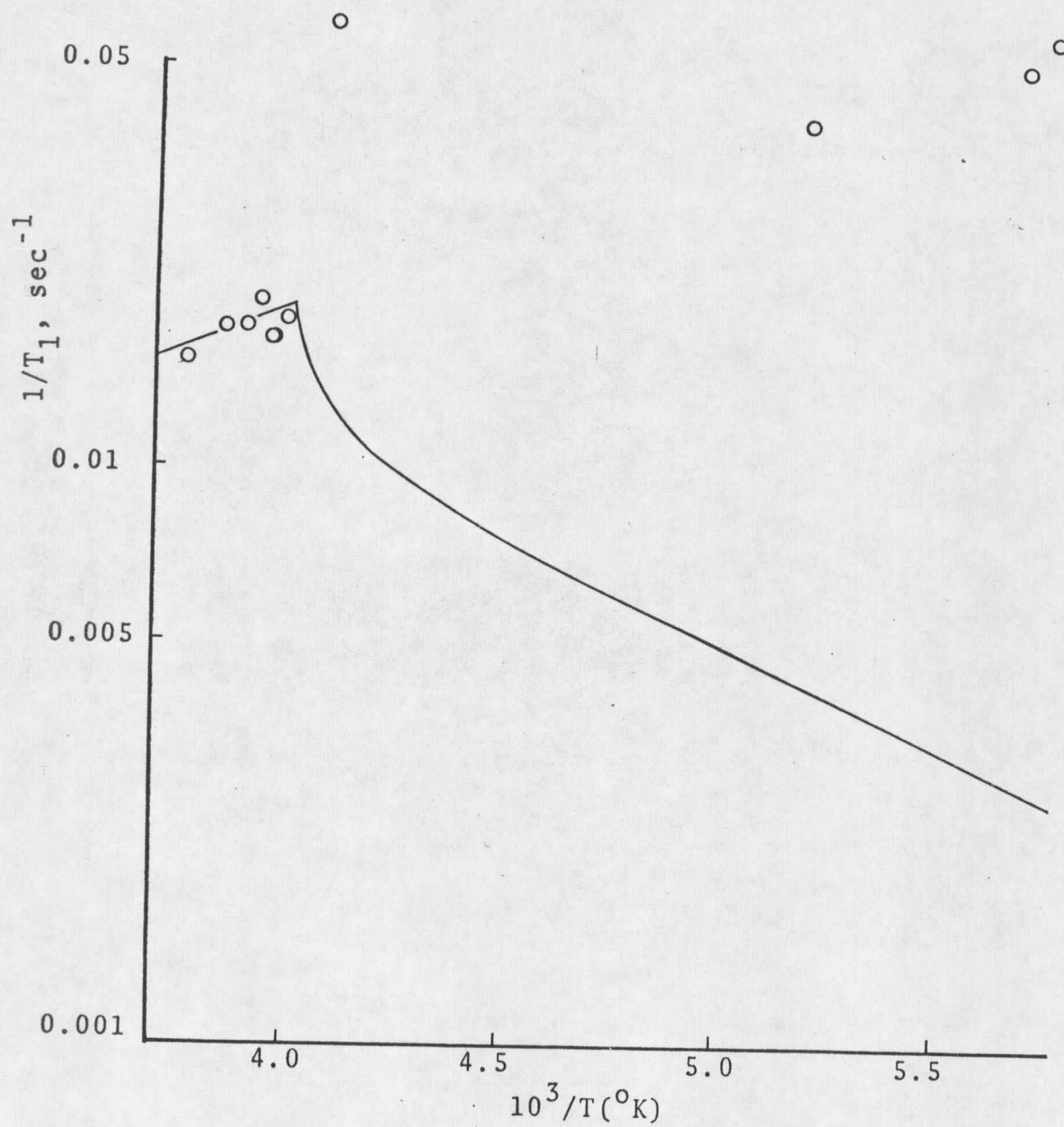


Figure 27: $D T_1$ Data Compared to $J(\omega) \propto (1 - p^2)$

attributed to a quadrupolar interaction between the Na^{23} and the lattice which becomes very strong in a region of about 30°C around the transition. T_1 drops sharply, by nearly a factor of 10, then rises equally sharply below the transition. The deuteron and sodium T_1 observed here (Figs. 25 and 26) shorten fairly sharply but do not lengthen very sharply below the transition.

Since such soft lattice modes and deuteron interbond and intrabond motion are not contributing much to T_1 below the transition, the effect of lattice vibrations over the whole temperature range below T_c to 80°K will be considered.

Several theories of this sort are available. Van Kranendonk has considered harmonic⁽⁴⁸⁾ and anharmonic⁽⁴⁹⁾ phonon contributions to nuclear relaxation. Chang has developed a theory⁽⁵⁰⁾ for the nuclear relaxation of Cl in NaClO_3 . He assumes that the field gradient set up by the three oxygens and modulated by a Debye spectrum of phonons is responsible for the Cl^{35} relaxation. Bayer⁽⁵¹⁾ has developed a theory of relaxation for Cl^{35} in $\text{C}_2\text{H}_2\text{Cl}_2$ molecular crystals which assumes relaxation by molecular rotation rather than by lattice vibrations.

The lattice vibration theories of Van Kranendonk and Chang ultimately predict dependence of $1/T_1$ on the square

of the temperature. The deuteron data from Fig. 25 is plotted in Fig. 28, without distinction as to frequency at which the measurement was made, as $\log 1/T_1$ vs $\log T$. Lines of slope 2 and slope 3.38 are drawn to illustrate the possibility of fitting $1/T_1$ to a power of the temperature. The data is clearly not linear, but a best fit indicates T^3 or stronger dependence. No attempt to quantitatively compare these lattice vibration theories to this deuteron data has been made.

Since Myasnikova and Arefev⁽²²⁾ have observed several bands which are at low enough energy to be torsional oscillations of the SeO_3 group, it is worth investigating the applicability of Bayer's theory to this crystal. This theory assumes that the torsional molecular oscillator can attain several excited states, as well as the ground state, but that only transitions between excited states and the ground state occur, i.e., transitions between two excited levels occur only via the ground state. It further assumes that the phase of the oscillator as it enters a new state is random. This produces random rotations of the efg tensor about the rotation axis, and hence at the site of the nucleus. The frequency spectrum of this random motion includes components at the resonant frequency and

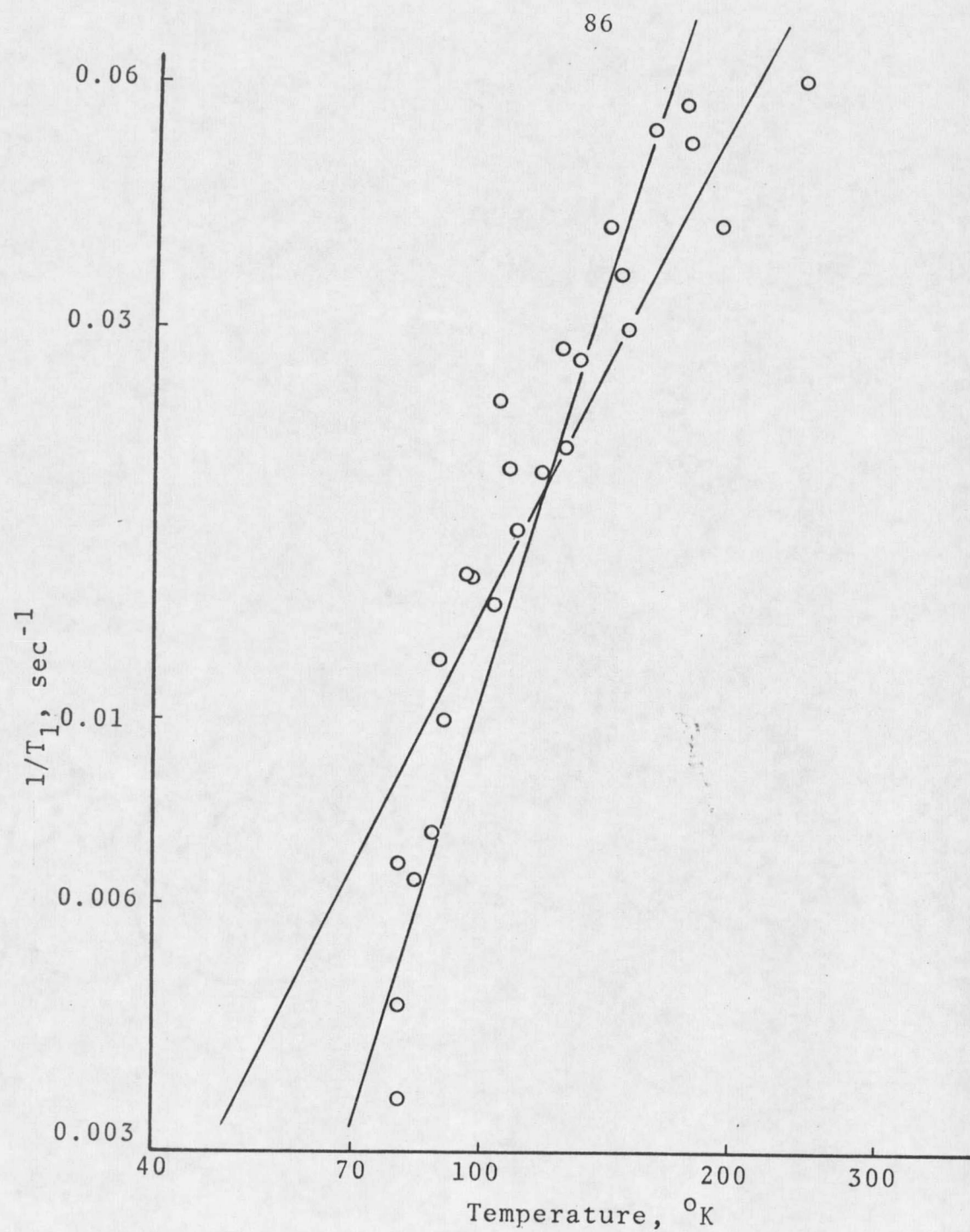


Figure 28: Log-log Plot of Reciprocal of D
 T_1 vs Temperature

at twice the resonant frequency, which can cause $\Delta m = \pm 1$ and $\Delta m = \pm 2$ transitions. If we assume that the mean lifetime of a state (τ_a) is at least slightly longer than a vibration period ($1/\nu_t$) of the oscillator, the term $4\pi^2 \nu^2 \tau_a^2 \gg 1$ and Bayer's expression for the $\Delta m = \pm 2$ transition probability becomes

$$W_2 = \frac{3}{8} \frac{h^2 \omega_Q^2 \tau_a}{\theta^2 \omega_t^2} \frac{4 \cosh x - 3}{(e^x - 1)^2} \quad (27)$$

where $\nu_Q = \frac{\omega_Q}{2\pi}$ is the quadrupolar splitting frequency of the nucleus due to the efg tensor at its site, $\nu_t = \omega_t/2\pi$ is the ground state frequency of the torsional oscillator, $x = h\nu_t/kT$, and θ is the moment of inertia of the molecular oscillator.

Woessner and Gutowsky⁽⁵²⁾ have improved on Bayer's assumption that the lifetime in each excited state is the same by taking an average over the lifetimes in all excited states, using a result of Montroll and Shuler.⁽⁵³⁾

Their results are as follows:

$$W_2 = \frac{3}{64} \frac{h\omega_Q^2}{\theta\omega_t} \frac{\tau_a}{\sinh^4(x/2)}, \quad (28)$$

$$W_1 = \frac{3}{2} \frac{h\omega_Q^2}{\theta\omega_t^3} \frac{\coth(x/2)}{\tau_a} \quad (29)^{17}$$

The symbols are the same as those used in Eq. (27).¹⁷ Using $\theta = 1.8 \times 10^{-38}$ gm-cm² for SeO₃, $\omega_Q = 135$ kHz and $\tau_a = 5 \times 10^{-13}$ sec, W_1 and W_2 , together with the deuteron T_1 data, have been plotted in Fig. 29 for the lowest energy (57 cm⁻¹) band observed in STSe⁽²²⁾ and for hypothetical 23 cm⁻¹ and 30 cm⁻¹ bands. From about 50°C below the transition to 80°K, the agreement between the temperature dependence of this theory and the data is somewhat better than the agreement between the data and the T^2 dependence illustrated in Fig. (28). Quantitative agreement in part of the region of measurement can be obtained by assuming a 23 cm⁻¹ band, and a mean excited state lifetime of 5×10^{-13} sec. However there is no other experimental evidence for these values.

To explain the deuteron and sodium T_1 measurements obtained below T_c , especially the fact that the magnitude of T_1 becomes shorter just below T_c , it seems that some sort of fluctuations of the lattice or molecular groups will have to be invoked. These fluctuations will have to be treated differently than lattice fluctuations have

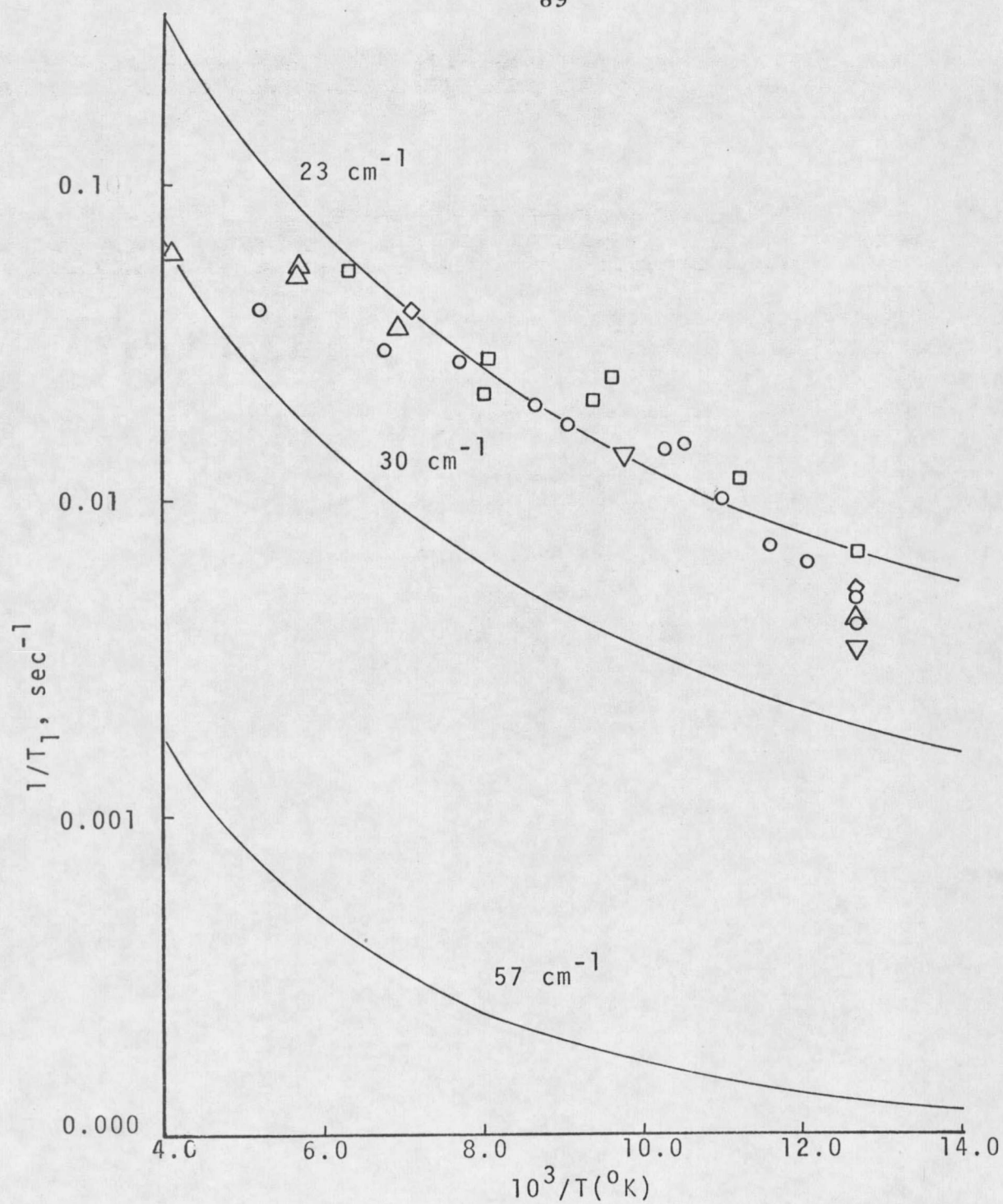


Figure 29: Deuteron T_1 Data Compared to Torsional Oscillation Theory Contributions

been to explain shorter T_1 values of nuclei in other crystals. (44,47) While the treatment of torsional oscillations described above does not adequately account for the data, it is nevertheless likely that torsional oscillations will be important in the motions which describe this relaxation data. This is because the ordering of deuterons in preferred ends of bonds is likely to change the characteristic motions of the SeO_3 groups. Soda and Chiba⁽³⁰⁾ have accounted for their deuteron splitting in terms of the changing of the length of a hydrogen bond by a rotation of an SeO_3 group to a new equilibrium position below T_c . If a rotation of an SeO_3 group is a part of the displacement which occurs with the ferroelectric state, large fluctuations of the group between the equilibrium positions is likely to occur in the vicinity of the transition. (This is discussed with reference to KH_2PO_4 by Cochran.⁽⁵⁴⁾) Thus, if the presence of a torsional mode in the vicinity of 23 cm^{-1} can be verified, random fluctuations of a torsional mode of the SeO_3 group offer some possibility of accounting for the T_1 data observed.

CHAPTER VI: DISCUSSION OF RESULTS

From the T_1 measurements and conductivity measurements made in this investigation, activation energies for two types of deuteron motion above the Curie temperature have been obtained. One, considered to be deuteron intrabond motion, was found to have an activation energy of 0.055 ± 0.01 eV. This motion was found to be largely responsible for the deuteron spin-lattice relaxation from room temperature down to the Curie temperature, and appears also to be responsible for the relaxation of Na^{23} nuclei in this temperature range. The other, considered to be deuteron interbond motion, was found to have an activation energy in the range of 0.65 to 0.85 eV. These values were obtained by deuteron spin-lattice relaxation time measurements and by electrical conductivity measurements. The variation in values is due to the conductivity activation energy being somewhat different along the different axes, and due to fairly large uncertainties in the T_1 measurements. The jump time associated with this motion was measured over the temperature range from 50°C to -15°C . An activation energy of 0.73 ± 0.07 eV was obtained from these measurements. This value agrees well with the values obtained from conductivity and T_1 measurements. At 30°C ,

the pre-exponential factor applicable to the jump time is 2.3×10^{-13} sec, which is close to the value of h/kT as expected.

The temperature and frequency dependence of the Na^{23} T_1 in the temperature range from 310 to 360°K was compared to predicted T_1 results due to the effect of deuteron interbond motion. It was shown that the observed frequency dependence of the Na^{23} T_1 implies that deuterons are trapped in the vicinity of a particular Na^{23} nucleus for a time long compared to the Na^{23} Larmor frequency. In this case, the activation energy for the Na^{23} T_1 should have the same value as for the deuteron T_1 and electrical conductivity. Such was not the case - the energy associated with the Na^{23} T_1 was only about half that of the deuteron T_1 .

Measurements of deuteron T_1 below the Curie temperature give no indication of either of the types of deuteron motion observed above T_c . From Fig. 13 one would expect that deuteron interbond motion would make negligible contribution to T_1 in this temperature range. The absence of evidence of intrabond motion in the temperature range just below T_c is in contrast to results observed in KD_2PO_4 .⁽⁴⁶⁾ Apparently, however, below T_c , in DSTSe another relaxation mechanism related to lattice vibrations or molecular

oscillations becomes more important and masks any evidence of a deuteron intrabond motion contribution. At the onset of the ferroelectric transition the T_1 of deuteron and sodium nuclei shortered, then eventually lengthened slowly as the crystal was cooled further. It is believed that the T_1 of these nuclei is due to the same motion or fluctuations of a type of motion, because of the similar temperature and frequency dependence of the relaxation times of the two nuclei. However, this shortening of T_1 in the region of the transition is neither large enough nor confined to a narrow enough temperature range to be considered to be due to the softening of a ferroelectric mode as observed by Blinc and Zumer⁽⁴⁷⁾ in p^{31} relaxation in KH_2PO_4 or by Rigamonti⁽⁴⁴⁾ in Na^{23} relaxation in NaNO_2 . It is not entirely clear over which part of the temperature range from T_c down to 80°K , the relaxation processes are due to the phase transition itself and over which part of the range a mechanism characteristic of the lower phase, rather than the transition, is responsible for the observed values of T_1 of both nuclei. Since the crystals were not entirely deuterated (75 to 87% deuterons), the phase transition and its effect on T_1 may extend over a substantial temperature range. The fact that the deuteron

NMR lines exhibit a poor signal to noise ratio for 20° to 40°C below the transition may be another manifestation of such an effect. If such is the case, the values of T_1 of both nuclei in the 40°C region below T_c where the values of T_1 are roughly constant would be due to a different mechanism than the values from about 200°K to 80°K , where the log of $1/T_1$ is roughly linear with $1/T$, with slope of about 0.025 eV . In this latter region the torsional mode calculation can be made to predict the deuteron T_1 data in a general way.

To further understand these results, it would be useful to investigate the spin-lattice relaxation times of deuteron and lithium nuclei in $\text{LiD}_3(\text{SeO}_3)_2$. This crystal is similar to $\text{NaD}_3(\text{SeO}_3)_2$ but it is ferroelectric over its whole temperature range, from its melting point at 110°C down. If the deuterons order in the hydrogen bonds, the intrabond motion contribution to deuteron and sodium T_1 observed in DSTSe in the $+25^{\circ}\text{C}$ to -25°C range, would be absent in DLTSe. The T_1 behavior in the transition region of DSTSe would also be absent. Two relaxation mechanisms would be expected to be important - deuteron interbond jumping in the higher temperature range, and some mechanism similar to that observed in DSTSe well below T_c . Because no transition occurs in DLTSe, this lower tempera-

ture mechanism might govern T_1 over a wider temperature range than in DSTSe, so this mechanism would be easier to analyze. By comparison to the Li^7 and $\text{D } T_1$ data, it might also be clearer what part of the D and Na^{23} T_1 data in DSTSe may be associated with critical fluctuations due to the change of phase and what part of the data is due only to motion allowed in the ferroelectric phase.

As previously discussed, the temperature and frequency deuteron T_1 from 20°C to the transition temperature is explainable by deuteron intrabond motion. Such motion is indicative of a dynamic disordering of the deuterons in their bonds in the paraelectric phase. There has been some previous suggestion from infrared studies⁽²⁴⁾ and from the second moment studies of the proton line⁽²⁸⁾ that the potential well in the paraelectric phase has a single potential minimum and therefore the protons can execute only very small amplitude intrabond vibrations. The deuteron NMR spectra^(29,30) have been interpreted, as discussed in Chapter III, as evidence of dynamic disorder above T_c . If the hydrogen nuclei occupy centrally located minima, however, the direction of the ϕ_{yy} component of the efg tensor still would be expected to roughly bisect the perpendiculars to the two $\text{Se}-\text{O}\dots\text{O}$ planes of the bond. Therefore, the evidence of deuteron intrabond motion above T_c can be

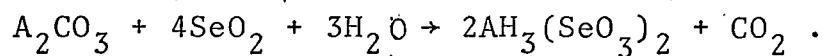
considered to lend stronger support to the order-disorder element of the phase transition in DSTSe.

In summarizing the results of his deuteron NMR measurements, Anderson⁽⁹⁾ concluded that because the efg tensors of the deuteron bonds in DSTSe changed more than they did in DKDP, the phase transition of DSTSe is less exclusively of the order-disorder type than that of DKDP. The comparison of deuteron T_1 behavior just below T_c with a similar study in DKDP (Fig. 27) indicates that the effect of polarization by deuteron ordering is not the dominant factor in the behavior of deuteron T_1 just below T_c - some additional motion or fluctuation, for which there is no equivalent phenomenon in DKDP, was observed to be important in this region.

CHAPTER VII: EXPERIMENTAL TECHNIQUE AND APPARATUS

SECTION I: Preparation of Samples

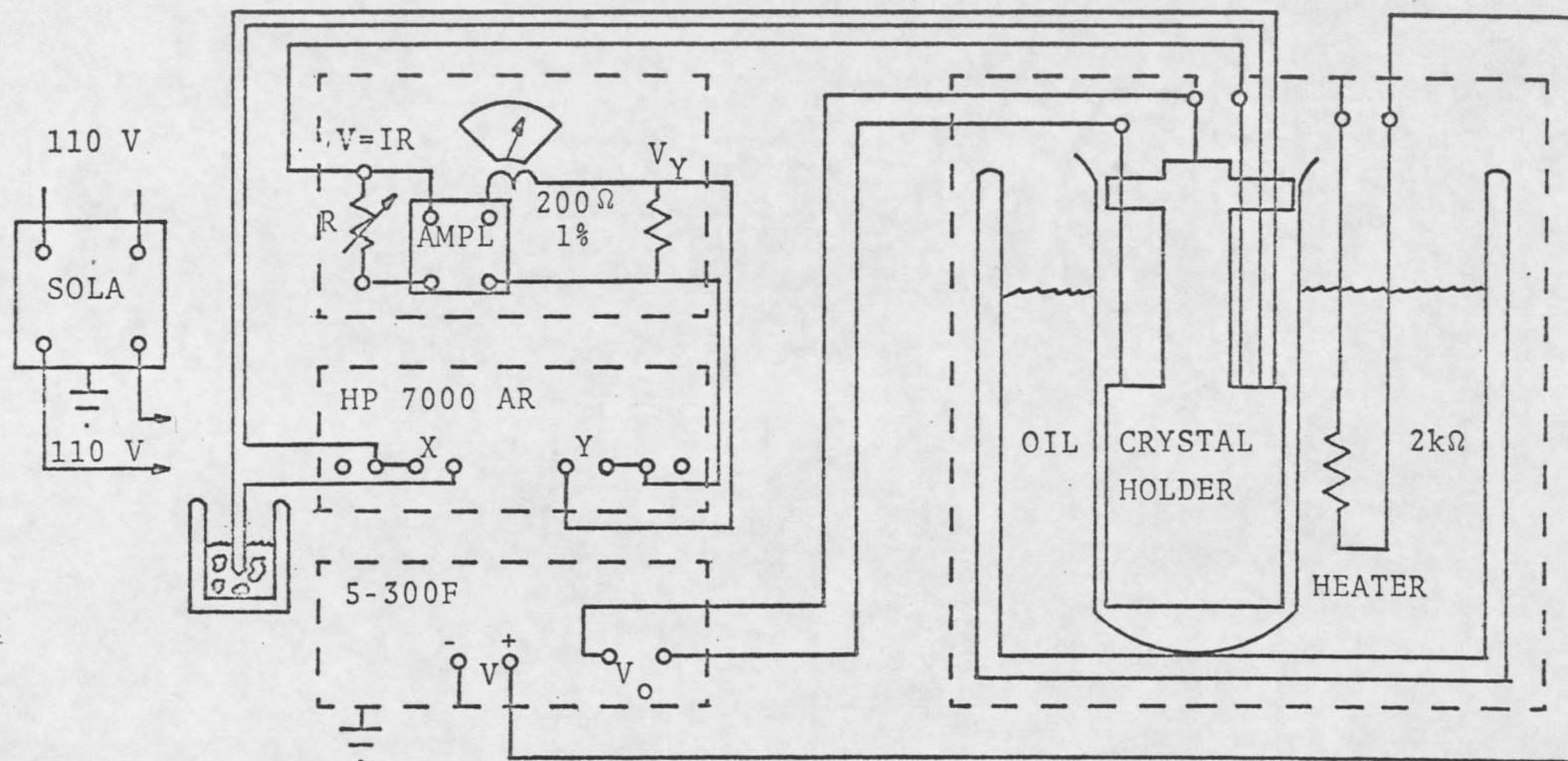
All samples of $\text{NaH}_3(\text{SeO}_3)_2$, $\text{NaD}_3(\text{SeO}_3)_2$ and analogous compounds with other alkali metals substituted for Na were grown by slow evaporation from aqueous solutions which were prepared from the alkali carbonate A_2CO_3 and selenium dioxide according to the reaction:



When used to prepare deuterated compounds, this technique allowed preparation by a reaction with D_2O (99%) in D_2O (99%) solvent so less than 1% of the hydrogen nuclei in the original solution are protons. The carbonate was dried in an oven overnight at 140°C to remove any water of hydration or adsorbed water. Nevertheless, crystals of only about 75 to 90% deuteration were obtained. Most of the protons came from $\text{D}_2\text{O} \leftrightarrow \text{H}_2\text{O}$ exchange with the atmosphere as the crystals were grown. Slight dilution (a few per cent per year, at most) may also occur through exchange at the surface of the crystal. Crystals of 0.5 to 5 cm^3 were grown in two to six weeks.

SECTION II: Electrical Conductivity

A schematic diagram of the conductivity measurement apparatus is given in Fig. 30. Various power supplies, including a Fluke 881A dc differential voltmeter supplying up to 10 volts, a Lunar Model 150-1 Regulated Supply for the 5 to 30 volt range, and a Dressen-Barnes 5-300F Regulated supply for the 30-300 volt range, were used to pass current through the crystal. The current level was kept low enough, and the polarity reversed often enough, that the amount of current passed through the crystal in one direction never involved as many carriers as are contained in a monolayer of area equal to that of the contact. This condition was adhered to because depletion of the layer just under the contact can create a barrier which introduces error in the conductivity measurement. Either a General Radio 1230-A Electrometer or a Keithley 148 Nanovoltmeter was used to measure the current through the crystal. The applied voltage was monitored with the Fluke differential voltmeter. Current and temperature were recorded on the Y and X axes of the H.P. Moseley 7000 AR X-Y Plotter. A chromel-alumel thermocouple with an ice bath reference monitored the temperature. The crystal holder, thermocouple, and leads are illustrated



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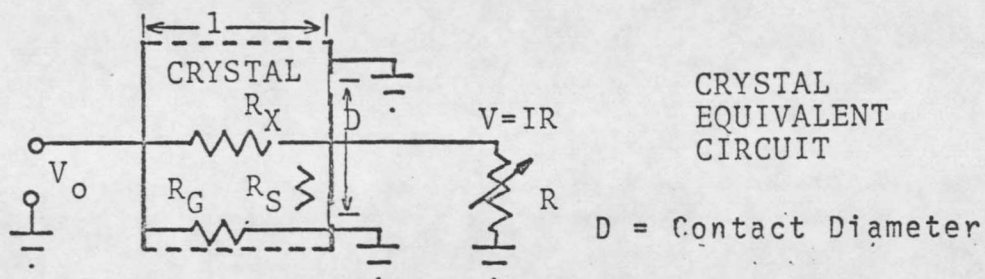


Figure 30: Conductivity Apparatus

in Fig. 31. The sample and holder were surrounded by a copper cylinder and the entire sample holder was inserted in a Pyrex test tube. For measurements above room temperature this test tube was inserted in a thermos bottle containing mineral oil. The temperature was raised by passing current through a $2K\Omega$ power resistor hanging in the bottle. For measurements below room temperature, the test tube with sample holder sat in a thermos bottle of methyl alcohol. Small amounts of liquid air were added to the alcohol to cool the sample. To prevent condensation of moisture on the sample as it was cooled below room temperature, a thermos bottle of liquid air was connected by a hose to the crystal sample holder. The boil-off maintained a dry atmosphere about the crystal. The thermocouple was located near but not in contact with the sample. This reduced electrical noise but necessitated care in making sure sufficient time had lapsed for crystal and thermocouple to come to thermal equilibrium. Preparation of the sample consisted of cutting the crystal to the desired shape with a wet string, polishing the faces slightly by rubbing them lightly across a wet filter paper on a flat surface, measuring with a micrometer the thickness of the sample in the direction along which the field is to be

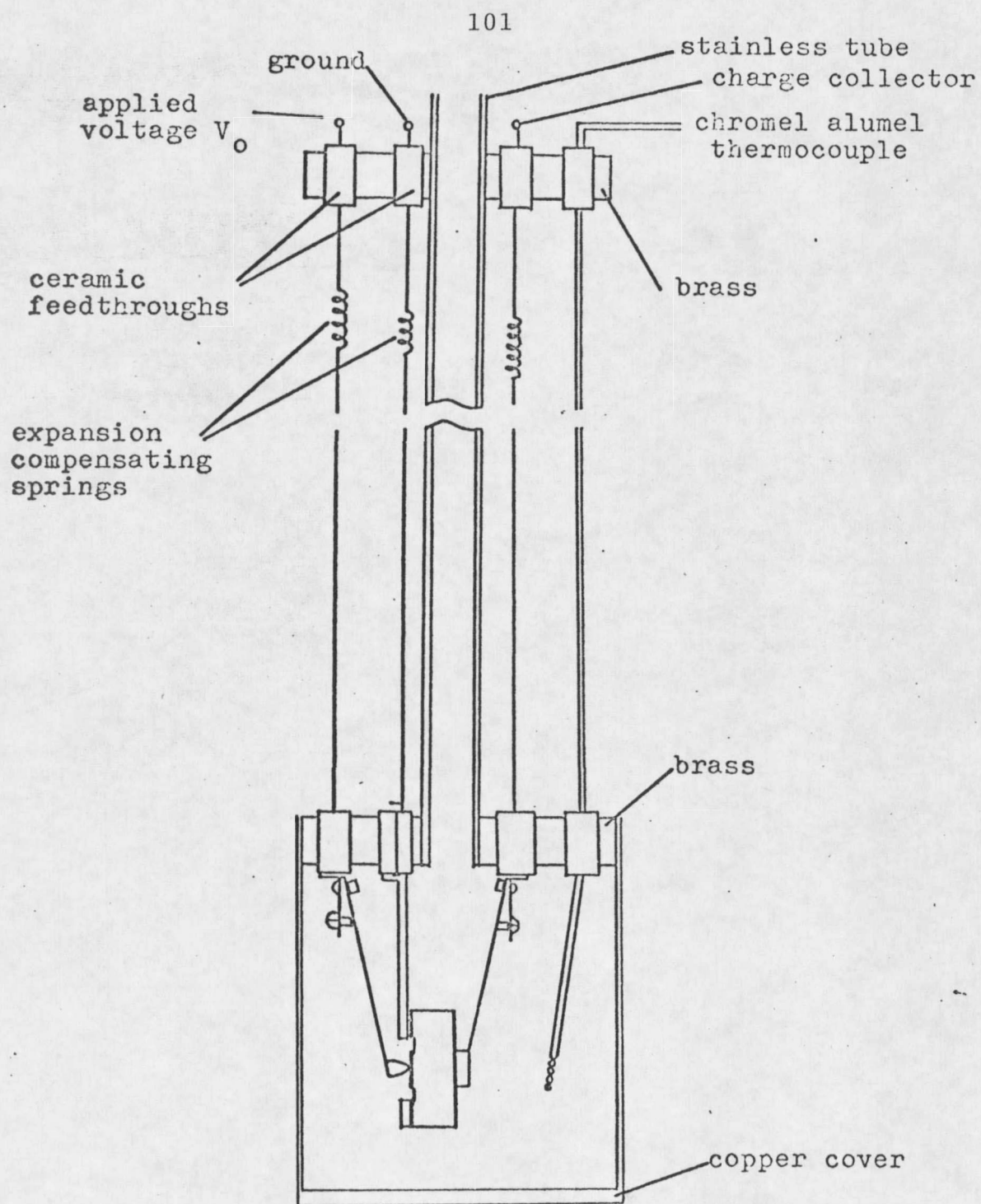


Figure 31: . Detail of Crystal Holder for Conductivity

applied, painting* contacts and guard ring, and measuring the contact diameter with a travelling microscope. Generally the contact and guard ring were inspected with the 30X binocular microscope: if there was not good separation between the contact and guard ring, a steel phonograph needle was used to scratch out the paint connecting the two.

Using the notation of Fig. 30,

$$\sigma = \frac{1}{A} \frac{I + IR/R_s}{V_o - V} \quad (30)$$

The resistance R across which the electrometer measures the voltage should be small enough that

$$R \ll R_s \quad (31a)$$

$$\text{and } V = IR \ll V_o. \quad (31b)$$

$$\text{Then } \sigma = \frac{1}{A} \frac{1}{V_o}. \quad (32)$$

The output V_Y of the electrometer equals a constant $K(s)$ times the input, where the constant $K(s)$ depends on the electrometer scale one is using. Therefore

* Dupont electronic grade Silver preparation #4817 was used for the contacts. It can be thinned with amyl or butyl acetate and can be applied with a small brush.

$$\sigma = \frac{1}{A} \frac{KV_Y}{RV_O}. \quad (33)$$

The conditions (31,a,b) held and Eq. (33) was used to analyze all data.

SECTION III: Continuous Wave (CW) Spectrometer

Deuteron NMR spectra and all T_1 measurements longer than about 20 seconds were made using a Robinson-type⁽⁵⁵⁾ variable frequency spectrometer with frequency modulation.⁽⁵⁶⁾ The circuit was built in a cylindrical brass can with five shielded compartments, one for the tuning capacitor, one for each amplifier stage, and one for the limiter stage.

A dc voltage of 5.0 to 5.5 volts, negative with respect to the spectrometer ground, was supplied to the filaments by a Nobatron Model QB6-2 Power Supply. A home-built dc power supply, closely resembling a General Radio Model 1204B, but with a pi filter ($L = 3.5h$, $C = 60\mu f$) added, provided a B^+ voltage of, generally, 235 volts, although 280 volts were used to obtain a high (one to two volts) radio frequency level on the coil. These supplies were fed by a Stabiline Type IE 5101 voltage regulator to buffer the wildly fluctuating voltage provided to the Physics Building by the Montana Power Company. Modulation and phase-sensitive detection of the signal were provided by a PAR Model HR-8 Lock-In Detector. The signals or spectra were recorded on a Bristol Strip-Chart recorder or on the Moseley X-Y plotter (with the X axis driven by the

sweep of the Varian 15" magnet power supply). In the case of signals barely visible above the noise, the dc output of the HR-8 was fed into a VIDAR Model 240 voltage-to-frequency converter and the signal was recorded in a TMC Model 401D 400-Channel analyzer. This arrangement allowed repeated sweeps over the same spectrum to be added, theoretically improving the signal to noise ratio by the square root of the number of sweeps recorded. The multi-channel analyzer was automatically started at the same place each sweep by a pulse from the magnet power supply as it recycled.

For temperature-dependent studies above room temperature the arrangement in Fig. 32 was used. The coil of the resonant circuit was connected to the spectrometer via a rigid coaxial cable, the outer conductor of which was a thinwall stainless tube. An aluminum cylinder surrounded the crystal. Attached to it was a power resistor, to which current was supplied from a Hyperion regulated power supply. The coaxial cable and crystal were insulated by a double-walled evacuated stainless tube.

For temperatures somewhat below room temperature, from about 25°C to -75°C, a large (1½" dia x 18") aluminum rod was attached to the lower end of the aluminum can

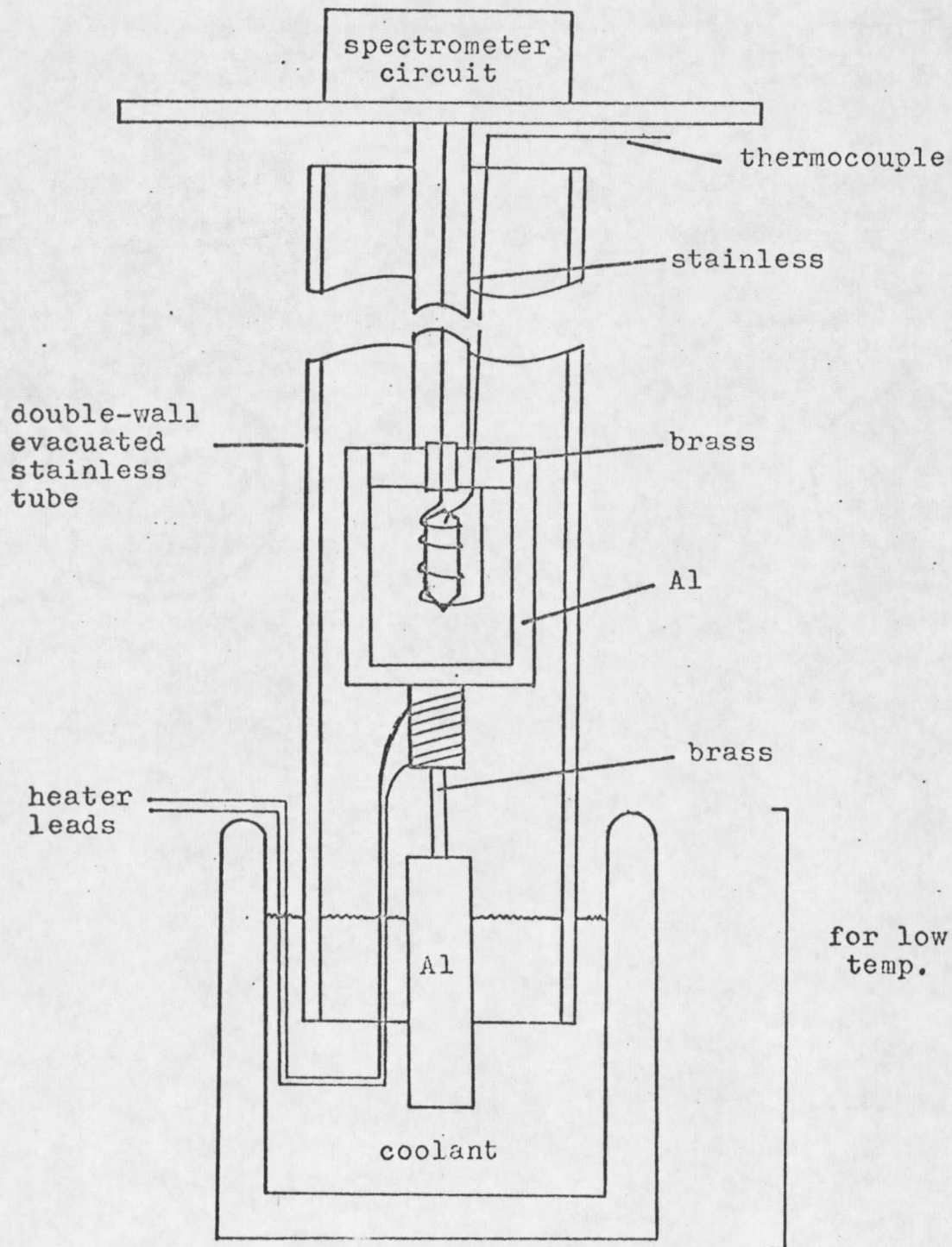


Figure 32: Temperature Control
for Robinson Spectrometer

surrounding the crystal by means of a thin brass rod (5/16" to 1/2" dia x 4") threaded at either end. The aluminum rod was mostly submerged in a temperature bath consisting of a wide-mouth 6 liter Dewar filled with ice and water, dry ice and alcohol, or liquid air, depending on the desired temperature range (see Fig. 32). Temperatures in the range -65°C to -200°C were attained with the spectrometer tube illustrated in Fig. 33. Liquid air in the reservoir served as the cooling agent. The temperature could be varied by controlling the amount of heat dissipated in the resistance wire just above the crystal. This power level was controlled by a feedback signal from the thermocouple via a Leeds-Northrup Model 9834 Null Detector (Fig. 34). The power supply, built by Robert Parker, is similar to the Kepco voltage-regulated power supplies which can be programmed to provide a desired output.

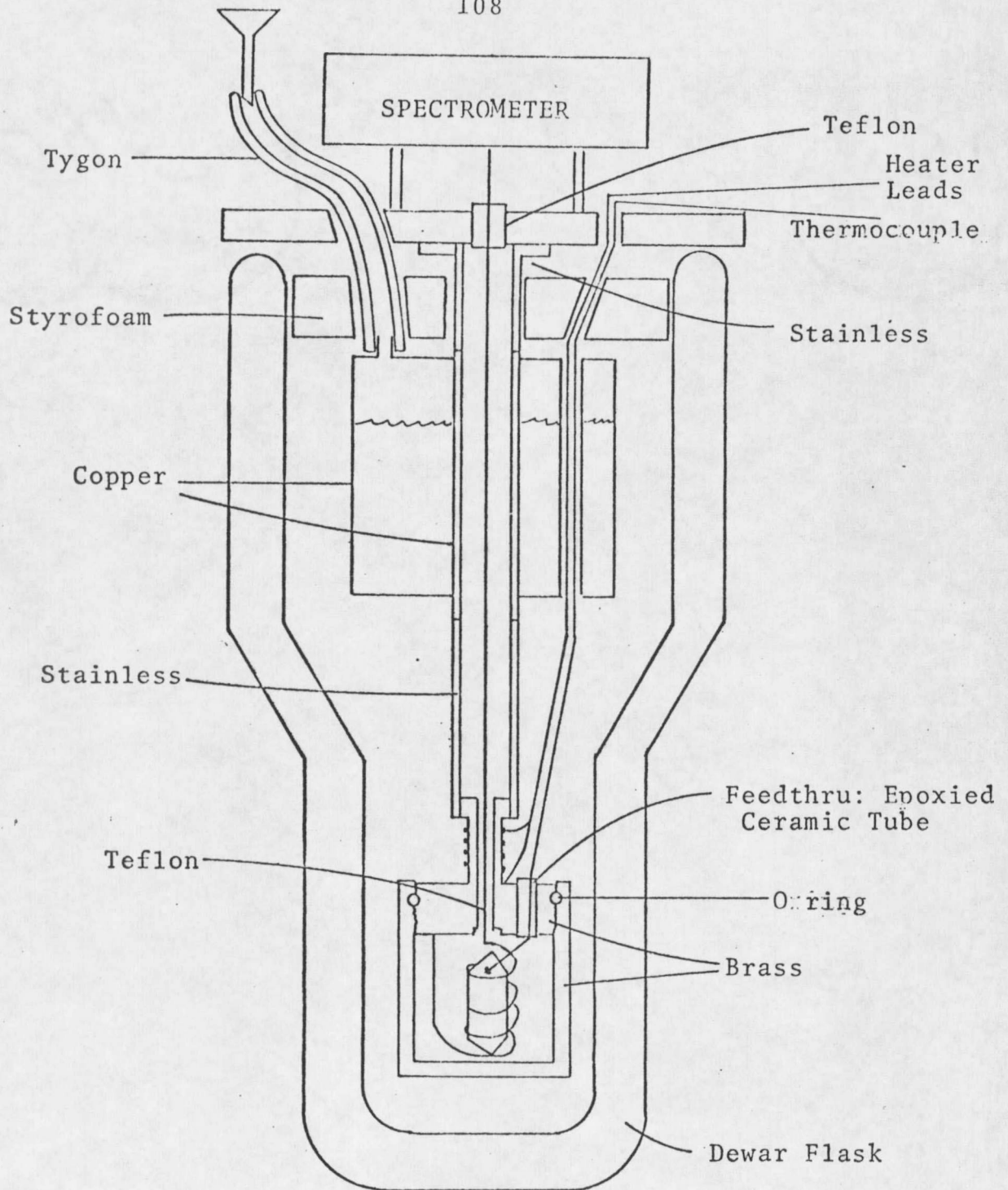


Figure 33: Low-Temperature Device
for Robinson Spectrometer

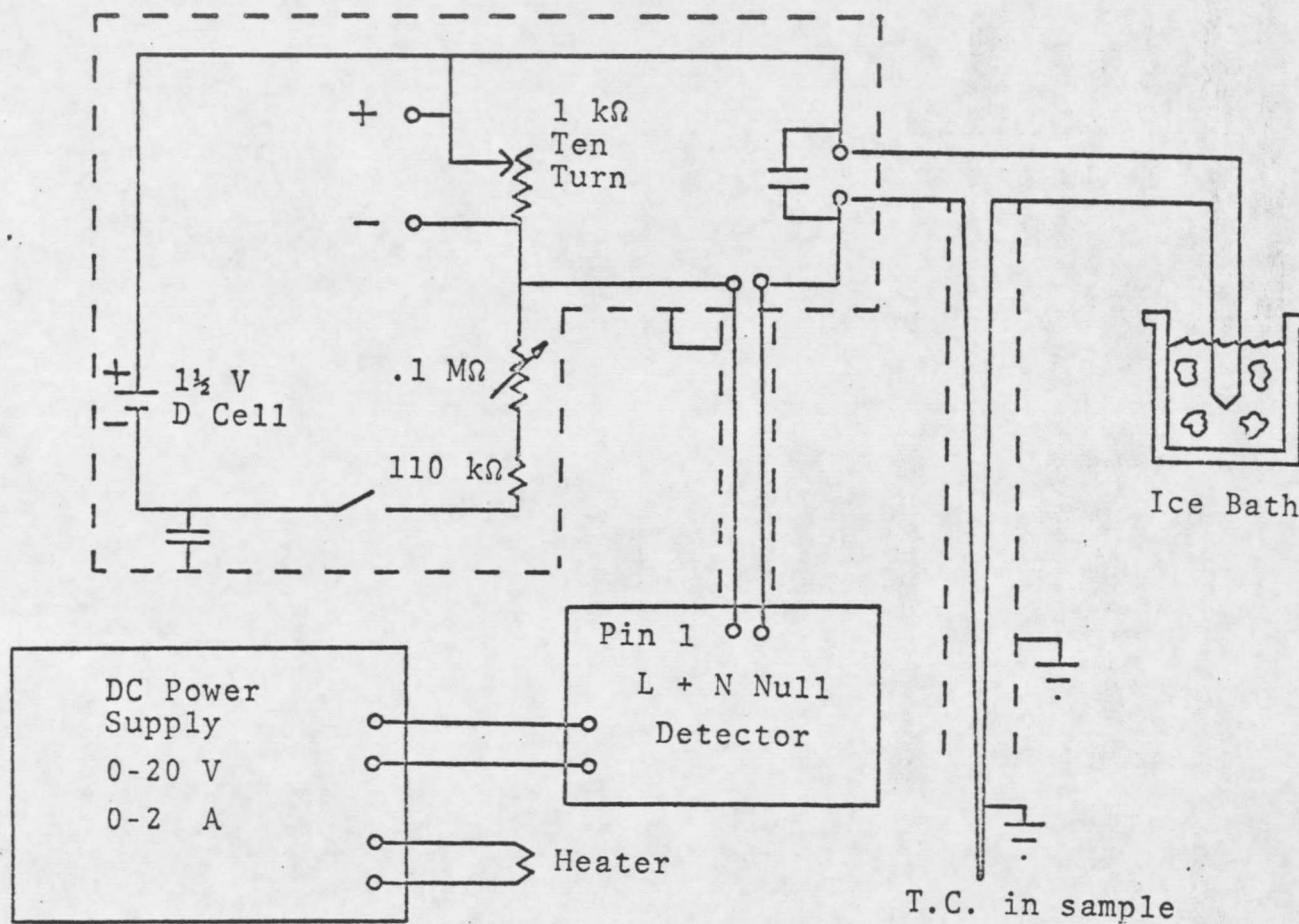


Figure 34: Temperature Control Apparatus

SECTION IV: Pulse Spectrometer

The pulse spectrometer built by Robert Parker and Fred Blankenburg consisted basically of a pulse generating and timing unit, a crystal-controlled (14.020 MHz) oscillator, a tuneable transmitter, an rf receiver, and a boxcar integrator for signal measurement. Fig. 35 illustrates the basic pulse spectrometer in block form. The pulse generator unit included the Tektronix Model 160A power supply, Model 162 wave form generator, and two Model 163 pulse generators. Pulses from less than 1 microsecond to 1 second could be supplied with any spacing up to 10 seconds. For the $90^\circ - \tau - 90^\circ$ two pulse experiments described previously, the pulse sequences were triggered externally by a unijunction timing circuit. The transmitter, receiver, and boxcar integrator are similar to those designed by Clark. (57,58) The transmitter coils were nearly Helmholtz in geometry and were part of a parallel resonant circuit. Maximum operating voltage applicable to the transmitter driving tubes was 2500 volts, which produced a deuteron 90° pulse length of slightly under 60 microseconds.

Fig. 36 illustrates the pulse head and crossed coil arrangement. Fig. 37 illustrates the teflon parts which

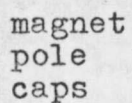


Figure 35: NMR Pulse Apparatus

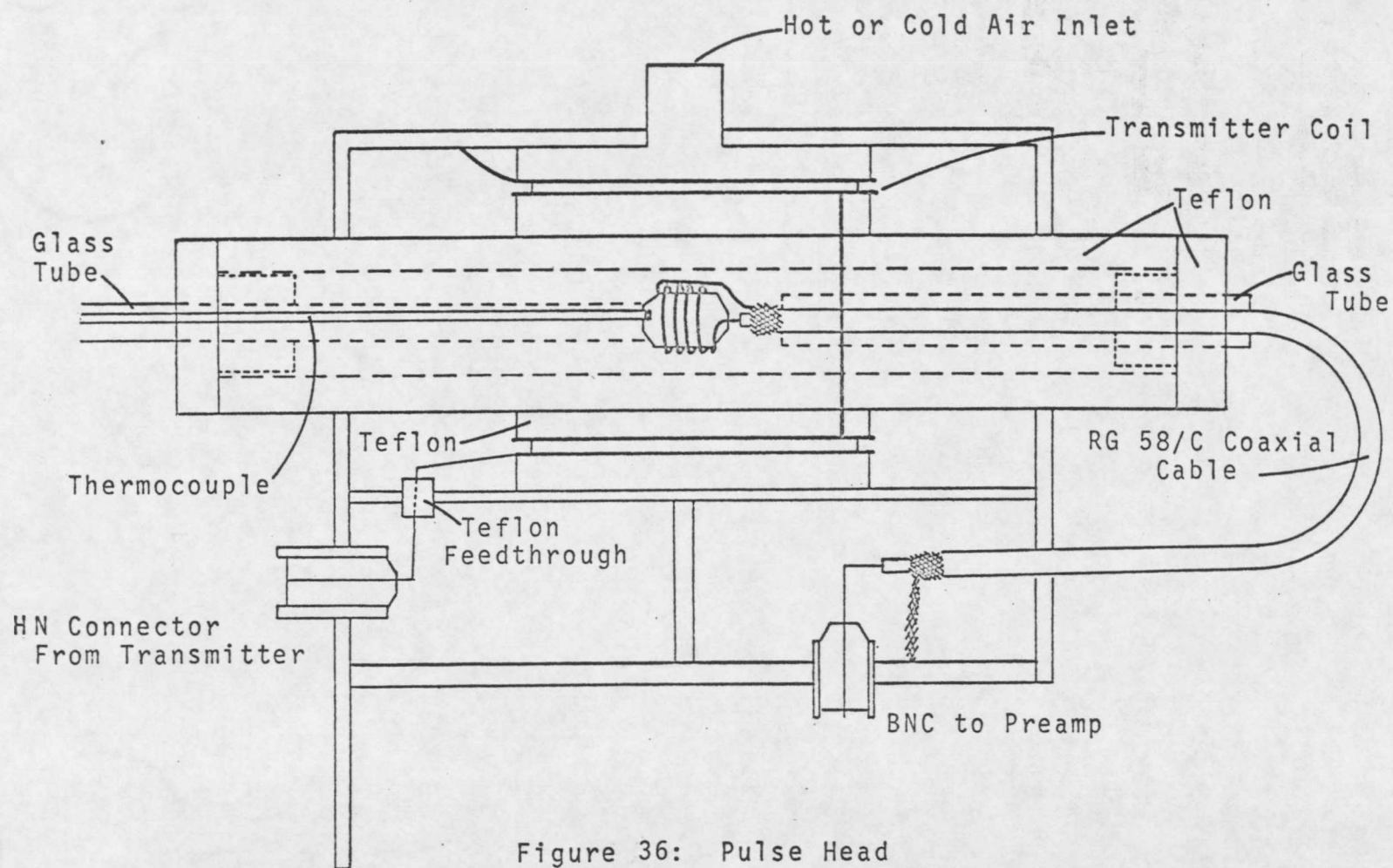


Figure 36: Pulse Head

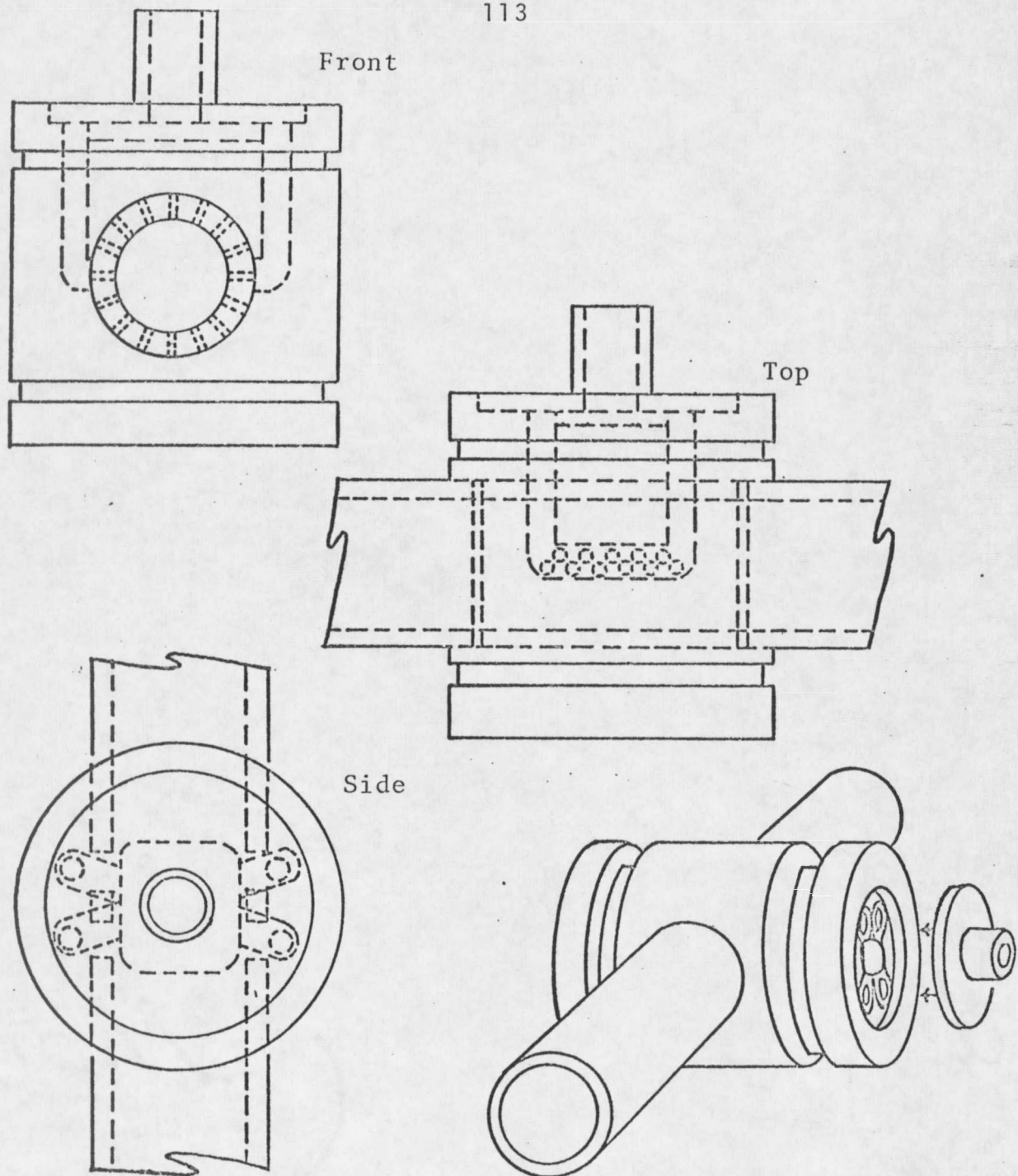


Figure 37: Detail of Gas Flow Inlets of Pulse Head

included the gas flow inlets. To attain temperatures above room temperature, a controlled flow of air, obtained by connecting the house compressed air line to a nitrogen gas-flow valve, was passed through a glass tube into the pulse head. Embedded in the glass tube was a heater element powered by a Variac. Adequate temperature stability was provided by running the Variac from the Stabiline Regulator. Temperatures below room temperature were attained in pulse experiments by controlling the boil-off rate of liquid air into the pulse head. Liquid air was boiled out of a narrow-neck Dewar through a double-walled evacuated glass or stainless transfer tube into the pulse head. The rate of boil-off was controlled by a feedback signal from a thermocouple in the crystal under study. The circuitry consisted of the Leeds-Northrup Null Detector and power supply described previously (Fig. 34).

SECTION V: CW T_1 Measurement Technique

The cw technique which gave the most reproducible results, and which was therefore used for the deuteron measurements in Figs. 13, 14, 15 and 25, involved the use of only the Robinson spectrometer. The circuit was tuned to a sufficiently high level that the spin system under study could be saturated or nearly saturated in a short time (1 - 2 min). After saturation, the magnetic field was changed by flipping the range switch to allow relaxation for a prescribed time (τ). Then the height of the resonance was observed by sweeping the magnetic field through the line. For complete saturation, the observed signals as a function of τ obey the relation

$$S(\tau) = S_0(1 - e^{-\tau/T_1}). \quad (34)$$

By plotting $\log (S(\tau) - S_0)$ vs τ , a straight line of slope $-1/T_1$ was obtained. However, particularly for relatively short T_1 values, complete saturation was not always attained. This did not introduce any error into the measurement if the same level of saturation was attained previous to each observation of the signal recovery, but it did give a less certain value of T_1 for the same mean square deviation of the experimental points from the best fit line.

APPENDIX

APPENDIX A: Contribution of Spin Diffusion to Paramagnetic Impurities to the Spin-Lattice Relaxation Time.

In order to calculate the possible contribution of the mechanism of spin diffusion to paramagnetic impurities to the deuteron T_1 in DSTSe, in the temperature range from 380°K to 80°K, we assume that all proton relaxation is via this mechanism, measure the proton T_1 in the same crystal (10 to 25% protons, 90 to 75% deuterons) and calculate the ratio of deuteron T_1 to proton T_1 theoretically. To make this calculation, we assume that the diffusion-limited case of the spin diffusion mechanism is applicable.*

The expression for T_1 in the diffusion-limited case is

$$\frac{1}{T_1} = 4\pi N\rho D \quad (A1)$$

where N = the impurity concentration

D = spin diffusion constant

$$\rho = .068(C/D)^{1/4}$$

* This assumption seems reasonable by comparison with results obtained by Eric Jones (39) in KH_2PO_4 . Here theory predicted relaxation in the diffusion limited case to well below 77°K and relaxation by the rapid diffusion case at liquid helium temperature, but the experimental results could be explained only in terms of the diffusion-limited case, over the whole temperature range from 4.2°K to 300°K.

$$\text{where } C = (2/5) \gamma_I^2 \gamma_e^2 h^2 S(S+1) \frac{\tau_e}{1 + \omega^2 \tau_e^2}, \quad (\text{A2})$$

where γ is the appropriate magneto-gyric ratio,

S is the spin quantum number of the impurity,

τ_e is the relaxation time for the electron,

ω is the Larmor frequency of the nucleus.

$$\text{The ratio } \frac{T_{1d}}{T_{1p}} = \frac{4\pi N \rho_p D_p}{4\pi N \rho_d D_d}, \quad (\text{A3})$$

where the d, p subscripts stand for deuteron and proton.

For the same crystal the N 's cancel. The parameter ρ contains C (Eq. A2), from which everything except the γ_I 's cancel if the experiment is done at the same frequency for the two nuclei (τ_e is nearly field-independent⁽³⁹⁾).

This leaves

$$T_{1d} = T_{1p} \frac{p_d^{3/4}}{d_d^{3/4}} \frac{p_p^{3/4}}{d_p^{3/4}}. \quad (\text{A4})$$

The problem now is to calculate the diffusion constant D for each nucleus.

$$D = a^2 W, \quad (\text{A5})$$

where a is the nearest neighbor distance and W is the mutual spin flip probability for nearest neighbors.

$$W = \frac{\pi}{10 \cdot 2^{1/2}} \frac{\gamma^4 h^2}{r_{12}^6} g(\omega_0), \quad (\text{A6})$$

where $r_{12} = a$ and

$$g(\omega_0) = 1/(2\pi\langle\Delta\omega^2\rangle)^{1/2}; \quad (A7)$$

$\langle\Delta\omega^2\rangle$ is the second moment of the line and equals

$$\frac{9}{20}\gamma_h^4 \sum_{ij} \frac{1}{r_{ij}^6} = \frac{9}{20}\gamma_h^4 \frac{8.5}{R^6} \quad (A8)$$

for a cubic array, where R is the internuclear spacing in the array.

Combining Eqs. (A5 - A8),

$$D = 0.14 \frac{\gamma_h^2}{R}, \quad (A9)$$

and Eq. (A4) becomes

$$T_{1d} = T_{1p} \frac{\gamma_p^2/R_p}{\gamma_d^2/R_d}^{3/4} \frac{\gamma_p^{1/2}}{\gamma_d^{1/2}} = T_{1p} \frac{R_d^{3/4}}{R_p} \frac{\gamma_p^2}{\gamma_d^2}. \quad (A10)$$

For the particular crystal under consideration T_c was at -23°C so the deuteron concentration was 87% and the proton concentration 13%.⁽⁴⁾ From the cell dimensions in Table I, $V \approx 290 \times 10^{-30} \text{ m}^3$. With six deuterons plus protons per cell, the volume per proton is $372 \times 10^{-30} \text{ m}^3$. This gives an inter-deuteron distance of $3.8 \text{ \AA}$ and an inter-proton distance at $7.2 \text{ \AA}$. Substituting these values,

$$T_{1d} = 26T_{1p}.$$

As discussed in Chapter IV, the deuteron T_1 values were actually several times shorter rather than 26 times

longer than the proton T_1 . If the crystal were actually 99% deuterons and 1% protons, the interproton distances would be $\approx 17\text{\AA}$ and the interdeuteron distances would be $\approx 3.6\text{\AA}$. Even in this case, from (A10), $T_{1d} = 10T_{1p}$. There is one additional correction to the deuteron internuclear distance which should be made, and it tends to make T_{1d} as calculated for this mechanism even longer. This correction involves realizing that there are inequivalent deuterons because of various quadrupolar interactions. Deuterons with different nuclear energy levels cannot execute mutual spin flips and still conserve energy. Therefore at temperatures low enough that interbond jumping is slow compared to the spin-diffusion contribution to T_1 , one should treat the energetically different types of deuterons as separate sublattices which do not interact for spin diffusion. This would lengthen the internuclear distance for each sublattice, and would thereby lengthen T_{1d} .

APPENDIX B: Spin-Lattice Relaxation via Quadrupolar Interaction

The following is an outline of the derivation of a general formula for quadrupolar relaxation of a spin 1 nucleus via random jumps which cause a randomly-changing field gradient.

One generally writes the Hamiltonian for the interaction as

$$H = \sum_q F^q(t) A^q, \quad (B1)$$

where $\sum_q$ is over all particles,

$F^q(t)$ incorporates all random functions of time for each particle and

A^q incorporates all time-independent coordinates and operators.

Then the transition rate is

$$W = h^{-2} |\langle \alpha | A | \beta \rangle|^2 \times J_{\alpha\beta}(\omega_{\alpha\beta}) \quad (B2)^*$$

$$J_{\alpha\beta}(\omega_{\alpha\beta}) = \int_{-\infty}^{\infty} G(\tau) \exp(-i\omega_{\alpha\beta}\tau) d\tau \quad (B3)$$

where $G(\tau)$ is the auto correlation function

$$G(\tau) \equiv \overline{F(t) F^*(t + \tau)}. \quad (B4)$$

The bar indicates an ensemble average over all particles and time average over the random time variable.

* This equation is developed in reference 59, section VIII C, page 272.

For the quadrupolar interaction

$$H = (3/2)a(3I_z^2 - I^2)V_0 + (I_+I_z + I_zI_+)V_{-1} + (I_-I_z + I_zI_-)V_{+1} \\ + (1/2)I_+^2V_{-2} + (1/2)I_-^2V_{+2} \quad (B5)$$

$$\text{where } a = \frac{eQ}{6I(2I-1)} = \frac{eQ}{6} \text{ for } I = 1 \quad (B6)$$

$$\text{and } V_0 = \phi_{zz}$$

$$V_{\pm 1} = \phi_{zz} \pm i\phi_{yz}$$

$$V_{\pm 2} = (\phi_{xx} - \phi_{yy}) \pm 2i\phi_{xy} \quad (B7)$$

where x, y, z are laboratory coordinates with z along the magnetic field, and the symbol $\phi_{x_i x_j}$ denotes $\frac{\partial^2 \phi}{\partial x_i \partial x_j}$

where ϕ is the electrostatic potential at the nuclear site.

We make the following identification with Eq. (B1):

$$\begin{aligned} A_1 &= (3/2)a(3I_z^2 - I^2) & F_1 &= V_0(t) \\ A_2 &= (3/2)a(I_+I_z + I_zI_+) & F_2 &= V_{-1}(t) \\ A_3 &= (3/2)a(I_-I_z + I_zI_-) & F_3 &= V_{+1}(t) \\ A_4 &= (3/4)aI_+^2 & F_4 &= V_{-2}(t) \\ A_5 &= (3/4)aI_-^2 & F_5 &= V_{+2}(t) \end{aligned} \quad (B8)$$

The spin-lattice relaxation time $1/T_1 = W_1 + 2W_2$ is calculated as follows: $W_1 = |\langle \psi_1 | H | \psi_2 \rangle|^2$ where $\psi = m - 1$, $\psi_2 = m$. The time independent part is

$$\begin{aligned}
& |(3/2)a\langle m|I_+I_z + I_zI_+|m-1\rangle|^2 \\
& = (9/4)a^2(2m-1)^2\{I(I+1) - m(m-1)\}, \\
& \text{which, for } I=1, = (9/4)\frac{e^2Q^2}{36} \times 2 = \frac{e^2Q^2}{8} \quad (B9a)
\end{aligned}$$

for W_2 , ($\Delta m = 2$), use A_4

$$\begin{aligned}
W_2 & = |(3/4)a\langle m|I_+^2|m-2\rangle|^2 \\
& = \frac{9e^2Q^2}{16 \times 36} [I(I+1) - (m-1)m][I(I+1) - (m-2)(m-1)] \\
& \text{which for } I=1, = \frac{e^2Q^2}{16} \quad (B9b)
\end{aligned}$$

$$\begin{aligned}
1/T_1 & = W_1 + 2W_2 = \frac{e^2Q^2}{8} J_{m,m+1}(\omega_{m,m+1}) \\
& + \frac{e^2Q^2}{8} J_{m,m+2}(\omega_{m,m+2}), \text{ where} \quad (B10)
\end{aligned}$$

$$\begin{aligned}
& J_{m,m+1}(\omega_{m,m+1}) \\
& = \int_{-\infty}^{\infty} F_2(t)F_2^*(t+\tau) \exp(-i\omega_{m,m+1}\tau) d\tau \quad \text{and}
\end{aligned}$$

$$\begin{aligned}
& J_{m,m+2}(\omega_{m,m+2}) \\
& = \int_{-\infty}^{\infty} F_4(t)F_4^*(t+\tau) \exp(-i\omega_{m,m+2}\tau) d\tau.
\end{aligned}$$

For random jumping between two sites, this average reduces, for $J_{m,m+1}$, to

$$\begin{aligned}
& (1/4)[\{\phi_{xz}(1) - \phi_{xz}(2)\}^2 + \{\phi_{yz}(1) - \phi_{yz}(2)\}^2] \exp(-|\tau|/\tau_c) \\
& \equiv (1/4)D_1 \exp(-|\tau|/\tau_c) \quad (B11a)
\end{aligned}$$

and, for $J_{m,m+2}$, to

$$\begin{aligned}
 (1/4) & \left\{ [\{\phi_{xx}(1) - \phi_{xx}(2)\} - \{\phi_{yy}(1) - \phi_{yy}(2)\}]^2 \right. \\
 & \left. + \{2\phi_{yx}(1) - 2\phi_{yx}(2)\}^2 \right\} \exp(-|\tau|/\tau_c) \\
 \equiv & (1/4) D_2 \exp(-|\tau|/\tau_c), \quad (B11b)
 \end{aligned}$$

if one assumes an exponential correlation function and

if $\omega_{m,m+1} \equiv \omega$ and $\omega_{m,m+2} \equiv 2\omega$.

Therefore, for jumping between two types of sites,

$$\begin{aligned}
 \frac{1}{T_1} &= \frac{e^2 Q^2}{8 h^2} \frac{1}{4} D_1 \int_{-\infty}^{\infty} e^{-i\omega\tau} e^{-|\tau|/\tau_c} d\tau \\
 &+ \frac{e^2 Q^2}{8 h^2} \frac{1}{4} D_2 \int_{-\infty}^{\infty} e^{-2i\omega\tau} e^{-|\tau|/\tau_c} d\tau \\
 &= \frac{e^2 Q^2}{16 h^2} \left(D_1 \frac{\tau_c}{1 + \omega^2 \tau_c^2} + D_2 \frac{\tau_c}{1 + 4\omega^2 \tau_c^2} \right) \quad (B12)
 \end{aligned}$$

When actually making calculations, values of $K\phi_{\alpha\beta}$,

rather than $\phi_{\alpha\beta}$, are available from experimental data,

where $K = \frac{3eQ}{2 h}$ (B13)

It is therefore useful to incorporate K^2 into the terms

D_1 and D_2 and divide by K^2 . Eq. (B12) then becomes

$$\frac{1}{T_1} = \frac{4(2\pi)^2}{9} \left(D_1 \frac{\tau_c}{1 + \omega^2 \tau_c^2} + D_2 \frac{\tau_c}{1 + 4\omega^2 \tau_c^2} \right) \quad (B14)$$

APPENDIX C: Calculation of Autocorrelation Function for Deuteron Interbond Jumping

The following calculation is applicable to either G_1 or G_2 , Eqs. (12a and 12b). For G_1 the functions F_2^i are used and for G_2 , the functions F_4^i are used. These F 's are defined in Eqs. (13a,b). The superscript "i" refers to the appropriate bond. To calculate G , one can assume that at $t = 0$, the deuteron is on an N^1 bond, and that at time τ , there are probabilities p_2 , p_3 and p_4 that the deuteron has jumped to S^1 , S^2 , N^2 respectively. Assuming that the rate of jumping to any of these bonds is W , and that the N bonds are twice as numerous as the S bonds, the equations for the probabilities are:*

$$\frac{dp_1}{dt} = W(2p_2 - p_1) + W(2p_3 - p_1) + 2W(p_4 - p_1) \quad (C1a)$$

$$\frac{dp_2}{dt} = W(p_1 - 2p_2) + W(p_3 - p_2) + W(p_4 - 2p_2) \quad (C1b)$$

$$\frac{dp_3}{dt} = W(p_1 - 2p_3) + W(p_2 - p_3) + W(p_4 - 2p_3) \quad (C1c)$$

$$\frac{dp_4}{dt} = 2W(p_1 - p_4) + W(2p_2 - p_4) + W(2p_3 - p_4) \quad (C1d)$$

* See ref. 60 for a short discussion of this technique of calculating correlation functions.

The solutions for the initial conditions $p_1 = 1$, $p_2 =$

$$p_3 = p_4 = 0 \text{ are: } p_1 = (1/3)(1 + 2e^{-6WT}) \quad (C2a)$$

$$p_2 = p_3 = (1/6)(1 - e^{-6WT}) \quad (C2b)$$

$$p_4 = (1/3)(1 - e^{-6WT}) \quad (C2c)$$

The contribution to the autocorrelation function for this initial condition (weighted $1/3$ because $1/3$ of the 6 bonds are N^1) is

$$(1/3)F^1 \{ (1/3)F^{1*}(1 + 2e^{-6WT}) + (1/6)F^{2*}(1 - e^{-6WT}) + (1/6)F^{3*}(1 - e^{-6WT}) + (1/3)F^{4*}(1 - e^{-6WT}) \} \quad (C3)$$

Similar calculations for the deuterons initially in each of the other types of bonds, weighted $1/3$ for N^2 and $1/6$ for S^1 and S^2 , yield a total autocorrelation function of

$$(1/36) \{ 4(F^1 - F^4)^2 + 2(F^1 - F^2)^2 + 2(F^1 - F^3)^2 + (F^2 - F^3)^2 + 2(F^2 - F^4)^2 + 2(F^3 - F^4)^2 \} \exp(-6 W\tau) + \text{const.} \quad (C4)$$

APPENDIX D: Spectral Density for Na^{23} Relaxation Due to Deuteron Interbond Motion

The electrical conductivity, σ , is assumed for simplicity to be due to one species of deuteron defect (vacant bond or excess deuteron), the other species being assumed immobile. The expression for the conductivity then is

$$\sigma = ne\mu, \quad (\text{D1})$$

where n is the mobile defect concentration, e is a protonic charge, and μ is the mobility. The concentration of defects is

$$n = N e^{-\frac{1}{2}E_n/kT}, \quad (\text{D2})$$

where N is the total number of deuteron bonds. This may be calculated as a statistical counting problem⁽⁴⁵⁾ or may be demonstrated by arguing that at equilibrium $\dot{n} = \text{number created/unit time} - \text{number destroyed/unit time} = 0$. Let T_0 be the normalizing time interval and b be the number of bonds nearest a deuteron site. Then

$$\begin{aligned} \dot{n} &= (N/T_0) \exp(-(E_n + E_m)/kT) \\ &\quad - n(bn/N) \exp(-E_m/kT) \times (1/bT_0) \\ &= 0. \end{aligned} \quad (\text{D3})$$

Then $n^2 = N^2 \exp(-E_n/kT)$, from which (D2) results.

For a mean jump distance a_0 , the mobility is given by

$$\mu = \frac{a_0^2 e \times \exp(-E_m/kT)}{b kT T_0} \quad (\text{D4})$$

Substituting into (D1),

$$\sigma = \frac{e^2 \exp[-(\frac{1}{2}E_n + E_m)/kT]}{b a_o kT T_o} \quad (D5)$$

Let τ_m be the mean time during which a carrier stays in the vicinity of a Na^{23} site and τ_n be the mean time between occurrences of a carrier by a particular Na^{23} site.

Assume $\tau_m \ll \tau_n$. Identify τ_n as the reciprocal of the rate constant in (D3)

$$\tau_n = \frac{N T_o}{n \exp(-E_m/kT)} = T_o \exp[(\frac{1}{2}E_n + E_m)/kT] \quad (D6)$$

Eqs. (D5) and (D6) relate σ and τ_n :

$$\sigma = e^2 / (b a_o kT \tau_n) \quad (D7)$$

$$\text{Assume } \tau_m = T_o \exp(E_m/kT) \quad (D8)$$

Calculate the correlation function

$$G(\tau) = \overline{F(0)F^*(\tau)} \quad (D9)$$

by drawing an analogy between this problem and the problem of intrabond jumping when a ferroelectric crystal is polarized with fractional polarization p .⁽⁴⁶⁾ In such a crystal, the proton or deuteron has a preferred end of its bond. The time between jumps to the wrong end of the bond is analogous to τ_n and the mean time it stays at the wrong end of the bond is analogous to τ_m . Then

$$\frac{1+p}{2} = \frac{\tau_n - \tau_m}{\tau_n}; \quad \frac{1-p}{2} = \frac{\tau_m}{\tau_n}; \quad p = 1 - 2 \frac{\tau_m}{\tau_n}, \quad (\text{D10})$$

and $G(\tau) = \frac{1}{4}(1 - p^2) \exp(-\tau/\tau_c)$ becomes $\frac{\tau_m}{\tau_n} \exp(-\tau/\tau_m)$

$$(\text{D11})$$

for $\tau_m \ll \tau_n$, and

$$J(\omega) = \frac{1}{4}(1 - p^2) \frac{\tau_c}{1 + \omega^2 \tau_c^2} \quad \text{becomes} \quad \frac{2\tau_m^2}{\tau_n}$$

$$\times \frac{1}{1 + \omega^2 \tau_m^2}. \quad (\text{D12})$$

APPENDIX E: Least Squares Best Fit of T_1 Data

The value of T_1 was obtained from the experimental observations S_i by making a best fit of the parameters A , B , and T_1 to the function

$$S(\tau) = A - B \exp(-\tau/T_1) \quad (E1)$$

by the method of least squares. An uncertainty in T_1 was then estimated.

An outline of this calculation follows. It is desired that the function

$$P \propto \exp \left[\sum_i \frac{\{S_i - S(\tau_i)\}^2}{2\sigma_i^2} \right] \quad (E2)$$

be maximal, where S_i is the observed signal at τ_i and $S(\tau_i) = A - B \exp(-\tau_i/T_1)$. For this calculation σ_i was assumed equal for all points so the function P is minimal when the mean square deviation is minimal.

$$\text{Dev.} = \sum_i \{S_i - S(\tau_i)\}^2 \quad (E3)$$

The conditions for this are

$$\frac{\partial \text{Dev}}{\partial A} = 0, \quad \frac{\partial \text{Dev}}{\partial B} = 0, \quad \frac{\partial \text{Dev}}{\partial (1/T_1)} = 0. \quad (E4)$$

These three conditions yield a transcendental equation which can be solved numerically. However, instead, since fairly good estimates of A , B , and T_1 can be obtained from

experimental data without doing a best fit, these equations were solved by letting

$$A \rightarrow S + \sigma, \quad B \rightarrow T + \theta, \quad 1/T_1 \rightarrow \Omega + \omega \quad (E5)$$

where S , T , and Ω are estimates of A , B , and $1/T_1$.

The equations (E4) are then linearized by expanding the exponential functions $\exp(-\tau_i/T_1)$ as $(1 - \omega\tau_i)\exp(-\Omega\tau_i)$

and neglecting all second order terms in a , b , and ω .

Equations (E4) reduce to

$$\sigma N - \theta \sum_i e^{-\Omega\tau_i} + T \omega \sum_i \tau_i e^{-\Omega\tau_i} = \sum_i S_i - NS + T \sum_i e^{-\Omega\tau_i} \quad (E6a)$$

$$-\sigma \sum_i e^{-\Omega\tau_i} + \theta \sum_i e^{-2\Omega\tau_i} + \omega \sum_i \tau_i e^{-\Omega\tau_i} (S - S_i - 2Te^{-\Omega\tau_i}) \\ = \sum_i e^{-\Omega\tau_i} (S - Te^{-\Omega\tau_i} - S_i) \quad (E6b)$$

$$\sigma T \sum_i \tau_i e^{-\Omega\tau_i} + \theta \sum_i \tau_i e^{-\Omega\tau_i} (S - S_i - 2Te^{-\Omega\tau_i}) \\ + \omega T \sum_i \tau_i^2 e^{-\Omega\tau_i} (S_i - S + 2Te^{-\Omega\tau_i}) \\ = T \sum_i \tau_i e^{-\Omega\tau_i} (S_i - S + Te^{-\Omega\tau_i}) \quad (E6c)$$

A computer program was written to do the sums, solve the linear equations for σ , θ , and ω . It added these values to S , T , and Ω to get better estimates of A , B , and $1/T_1$, and iterated the procedure for a specified number of cycles,

after which time the best values of A, B, and $1/T_1$ were obtained. (Four cycles were sufficient for almost all data fit in this manner.)

It is also desirable to obtain the standard deviation of T_1 obtained by this best fit procedure. This calculation is made by assuming that the distribution of curves one would obtain by best fitting various sets of data is Gaussian and that the probability P that a given curve $S_{oi} + \Delta_i$ is correct is

$$P \propto \exp - \frac{\sum_{i=1}^N [S_i - (S_{oi} + \Delta_i)]^2}{2\sigma^2} \quad (E7)$$

where S_{oi} is the best fit curve obtained by solving Eqs.(E6) to convergence and σ is the standard deviation of the points from this curve and is given by

$$\sigma = [\sum_i (S_i - S_{oi})^2 / (N - 3)]^{1/2} \quad (E8)$$

$$\Delta_i = \left. \frac{\partial S_o}{\partial A} \right|_{\tau_i} \Delta A + \left. \frac{\partial S_o}{\partial B} \right|_{\tau_i} \Delta B + \left. \frac{\partial S_o}{\partial (1/T_1)} \right|_{\tau_i} \Delta(1/T_1) \quad (E9)$$

Eq.(E7) may be rewritten as

$$P \propto \exp[-\sum_{i=1}^N (S_i - S_{oi})^2 / 2\sigma^2] \times \exp[-\sum_{i=1}^N \Delta_i^2 / 2\sigma^2] \\ \times \exp[\sum_{i=1}^N (S_i - S_{oi}) \Delta_i / 2\sigma^2] \quad (E10)$$

The first exponential is a constant which may be incor-

porated into the normalizing constant. The third consists of terms like $\sum_i 2(S_i - S_{oi}) \frac{\partial S_o}{\partial P} \Big|_{t_i}$ which equal zero by S_o being the best fit line. Therefore the term of interest is

$$P \propto \exp(-(\sum_i \Delta_i^2 / 2\sigma^2)) \quad (E11)$$

Using Eq. (E9), $\sum_i \Delta_i^2$ becomes: (where $W = 1/T_1$)

$$\begin{aligned} \sum_i \Delta_i^2 = & \sum_i \left(\frac{\partial S_o}{\partial A} \Big|_{\tau_i} \right)^2 (\Delta A)^2 + \sum_i \left(\frac{\partial S_o}{\partial B} \Big|_{\tau_i} \right)^2 (\Delta B)^2 \\ & + \sum_i \left(\frac{\partial S_o}{\partial W} \Big|_{\tau_i} \right)^2 (\Delta W)^2 \\ & + 2 \sum_i \left(\frac{\partial S_o}{\partial A} \Big|_{\tau_i} \right) \left(\frac{\partial S_o}{\partial B} \Big|_{\tau_i} \right) (\Delta A) (\Delta B) \\ & + 2 \sum_i \left(\frac{\partial S_o}{\partial A} \Big|_{\tau_i} \right) \left(\frac{\partial S_o}{\partial W} \Big|_{\tau_i} \right) (\Delta A) (\Delta W) \\ & + 2 \sum_i \left(\frac{\partial S_o}{\partial B} \Big|_{\tau_i} \right) \left(\frac{\partial S_o}{\partial W} \Big|_{\tau_i} \right) (\Delta B) (\Delta W) \end{aligned} \quad (E12)$$

Define the sums as follows:

$$\begin{aligned} \sum_i \Delta_i^2 = & L(\Delta A)^2 + M(\Delta B)^2 + N(\Delta W)^2 \\ & + P(\Delta A)(\Delta B) + Q(\Delta A)(\Delta W) + R(\Delta B)(\Delta W) \end{aligned} \quad (E13)$$

Now integrate over all ΔA and ΔB , to identify a standard deviation σ_W as the uncertainty in $1/T_1$.

$$P(\Delta W) = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \exp(-(\sum_i \Delta_i^2 / 2\sigma^2)) d(\Delta A) d(\Delta B) \quad (E14)$$

Integrate over ΔB by grouping the integral as:

$$\begin{aligned} P(\Delta W) &= \int_{-\infty}^{\infty} \exp[-\{L(\Delta A)^2 + N(\Delta W)^2 + Q(\Delta A)(\Delta W)\} / 2\sigma^2] \\ &\times \int_{-\infty}^{\infty} \exp^{-\frac{M}{2\sigma^2}[(\Delta B)^2 + \frac{1}{M}\{2P(\Delta A) + 2R(\Delta W)\}(\Delta B) \\ &\quad + \frac{1}{M^2}\{P(\Delta A)^2 + R(\Delta W)^2\}]} d(\Delta B) \\ &\times \exp \frac{1}{M^2}\{P(\Delta A)^2 + R(\Delta W)^2\} d(\Delta A) \end{aligned} \quad (E16)$$

$$\text{Define } U = \Delta B + \{P(\Delta A) + R(\Delta W)/M\} \quad (E17)$$

Then the center integral equals

$$\int_{-\infty}^{\infty} \exp(-MU^2/2\sigma^2) dU = \frac{1}{\sigma} (2\pi/M) \quad (E18)$$

The remaining integral can again be regrouped and integrated to yield:

$$\begin{aligned} 2\sigma^2 \pi (LM - P^2)^{-1/2} \exp[-\frac{1}{M}\{MN - R^2 - (MQ - PR)^2 / (LM - P^2)\} \\ \times (\Delta W)^2 / 2\sigma^2] \end{aligned} \quad (E18)$$

The pre-exponential may be incorporated into the normalizing constant. From (E18) we define σ_W , the uncertainty in $1/T_1$, by requiring (E18) to be of the form

$$\exp\{-\{(\Delta W)^2 / 2\sigma_W^2\} \quad (E19)$$

Therefore

$$\sigma_W = \sigma[(LM - P^2)/(2QPR + LMN - LR^2 - NP^2 - MQ^2)]^{1/2} \quad (E20)$$

The error bars in the T_1 measurements illustrated in Figs. 13, 14, 15, 21, 22, 23, 25 and 26 were calculated in this manner.

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