MONTANA STATE UNIVERSITY

Nuclear spin-lattice relaxation time measurement in NaD3(SeO3)2
by Roy Reinhart Knispel

A thesis submitted to the Graduate Faculty in partial fulfillment of the requirements for the degree of DOCTOR OF PHILOSOPHY in Physics
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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 Se03 groups to the spin-lattice relaxation time of the deuterons. The temperature and frequency dependence of the spin-lattice relaxation time of Na23 nuclei were similar to thqse of the deuterons over the same temperature and frequency ranges. The possibility of deuteron motion contributing to Na23 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 Na23 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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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 ($NaH_3(SeO_3)_2$ hereafter abbreviated STSe) and the contrasting properties of the deuterated analogue of this crystal ($NaD_3(SeO_3)_2$ 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 analagous 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, $LiH_3(SeO_3)_2$ 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

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*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 $NaH_3(SeO_3)_2$

	Paraelectric Phase $T > -79^oC$	Ferroelectric Phase I -79^oC to -172^oC	Ferroelectric Phase II $T < -172^oC$
Crystal Symmetry	Monoclinic 2/m	Triclinic 1	Monoclinic m
Space Group	$P\ 2_1/c$	C	
a cell dimension	10.36 A^o	20.60 A^o	10.4 A^o
b cell dimension	4.84 A^o	9.57 A^o	9.57 A^o
c cell dimension	5.80 A^o	5.76 A^o	5.75 A^o
Cell angle	90^o	$89^o36'$	90^o
Cell angle	$91^o10'$	91^o	
Cell angle	90^o	$90^o18'$	90^o

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

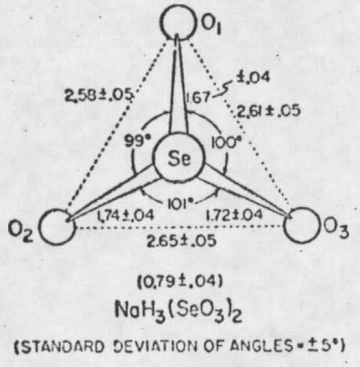

Figure 1: SeO_3 Pyramid in $NaH_3(SeO_3)_2$

(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 A^o) 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 A^o) 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, A^o	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.