A dielectric and nuclear magnetic resonance study of lithium hydrazinium sulfate and its deuterated isomorph

by Robert Sanford Parker

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Abstract:
Nuclear magnetic resonance measurements have been made on the Li7 spin system-in large single crystals of LiN2H5SO4. The Li7 relaxation time, T1, has been measured at 14 MHz for temperatures from 75 °K to 373 °K, and the ND2 deuteron T1 for temperatures from 100°K to 250°K. The activation energy for the observed relaxation in both the Li7 and ND2 deuteron relaxation for low temperatures is 0.20 ± .02 eV, as previously reported for NH3 and ND3 groups in the respective crystals. The Li7 and low temperature NDg deuteron relaxation accordingly results from hindered rotation of these groups, and is shown to be dipolar in all cases. The observed minimum T1's occur at 185°K and are 2.2 sec. in LiN2D5SO4, 0.52 sec. in LiN2H5SO4 and 4.0 sec. for ND2 deuterons. These data imply that the LiN2D5SO4 crystal was only 80% deuterated. Also measured were the Li7 quadrupolar coupling constant eqQ/h and asymmetry η in LiN2D5SO4. As temperature increases from 75°K to 447°K, eqQ/h decreases from 46.1 to 34.1 kHz and η decreases from 0.69 to 0.46.

Measurements were made of the pvroelectric coefficients in both LiN2H5SO4 and LiN2D5SO4 from 75°X to 150°K. The measured pyroelectric coefficients at 75°K are 11.4 ± 0.3 egs units for LiN2H5SO4 and 7.6 ± 0.1 egs units for LiN2D5SO4. The pyroelectric polarization is shown to be irreversible at 75°K confirming that both substances are not ferroelectric.

The observation of "hysteresis" loops has been shown to be consistent with a saturable dielectric. The model assumed is that of a series of periodically blocked channels along the c-axis. The complex dielectric constant of such a model is calculated and photographs of predicted behavior are shown. The inferred mean extrinsic barrier separation is from 6000 å to 15,000 å.

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ABSTRACT

Nuclear magnetic resonance measurements have been made on the Li^7 spin system in large single crystals of $LiN_2H_5SO_4$. The Li^7 relaxation time, T_1, has been measured at 14 MHz for temperatures from 75°K to 373°K, and the ND_2 deuteron T_1 for temperatures from 100°K to 250°K. The activation energy for the observed relaxation in both the Li^7 and ND_2 deuteron relaxation for low temperatures is 0.20 ± .02 eV, as previously reported for NH_3 and ND_3 groups in the respective crystals. The Li^7 and low temperature ND_2 deuteron relaxation accordingly results from hindered rotation of these groups, and is shown to be dipolar in all cases. The observed minimum T_1's occur at 185°K and are 2.2 sec. in $LiN_2D_5SO_4$, 0.52 sec. in $LiN_2H_5SO_4$ and 4.0 sec. for ND_2 deuterons. These data imply that the $LiN_2D_5SO_4$ crystal was only 80% deuterated. Also measured were the Li^7 quadrupolar coupling constant eqQ/h and asymmetry η in $LiN_2D_5SO_4$. As temperature increases from 75°K to 447°K, eqQ/h decreases from 46.1 to 34.1 kHz and η decreases from 0.69 to 0.46.

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Chapter I

INTRODUCTION

The compound lithium hydrazinium sulfate ($LiN_2H_5SO_4$), hereafter denoted LiHzS, was first prepared by Sommer and Weise[1] in 1916. The recent interest in both LiHzS and its deuterated isomorph $LiN_2D_5SO_4$ (LiDzS) was kindled by Pepinsky, et al.,[2] in 1958 when they reported their observation of what appeared to be ferroelectric hysteresis loops in LiHzS over the temperature range from $-15^{\circ}C$ to above $80^{\circ}C$. This placed LiHzS in a fairly small group of solids which are classed as hydrogen-bonded ferroelectrics. Generally, hydrogen-bonded ferroelectrics are studied as a means of gaining insight into the mechanics of hydrogen-bonding and the nature of the ferroelectric phase transition.

A good example of such a study has been the continued effort on KH_2PO_4 and KD_2PO_4 begun in about 1955 by Uehling and co-workers at the University of Washington[3,4,5] and continued today in several laboratories throughout the world. These studies have provided us with measurements of deuteron migration rates between hydrogen bonds and between the two stable deuteron locations within each hydrogen bond. The intrabond motion is related to the dielectric behavior and the sharpness of the phase transition while the interbond motion is responsible for the electrical conductivity.

"Ferroelectric" LiHzS and LiDzS have been the subjects of several

recent studies.[6-20] There have been several nuclear magnetic resonance (NMR) studies of the proton line width in LiHzS culminating in the rather extensive studies of the proton and Li^7 line width and spin-lattice relaxation done by Cuthbert and Petch[9] and the later studies done by MacClement, Pintar, and Petch[10] and by Knispel and Petch.[11] These workers all found evidence of molecular reorientation within the hydrazinium ($N_2H_5^+$) ion, but the assignment of the appropriate relaxation parameters could only be made by inference from similar phenomena in other crystals. This uncertainty was lifted by Howell and Schmidt[12,13] who completed a deuteron magnetic resonance study of LiDzS and concluded that the ND_2 and ND_3 groups rotate with an activation energy of 0.50 eV and 0.20 eV respectively. The high degree of correlation between these hindered rotation data is shown in Table I-1, taken from reference by Knispel and Petch.[11] In this work the electric field gradient tensor for the Li^7 nucleus in LiDzS has been measured and the Li^7 spin-lattice relaxation time has been measured. These NMR studies, along with the present work, are further discussed in Chapters II and IV.

The structure of LiHzS was obtained from a series of x-ray and neutron diffraction studies made from 1963 to 1967.[13,14,15] These studies revealed a structure consisting of channels formed by interconnected LiO_4 groups and SO_4 groups winding spirally along the c-axis (Fig.I-1a). Within these channels are chains of hydrazinium

TABLE I-1

MOTIONAL CORRELATION TIME PARAMETERS FOR $Li(N_2H_5)SO_4$ AND FOR $Li(N_2D_5)\ SO_4$

Motion	τ_o(sec)	E_a (eV)	Workers
NH_3^+ rotation	5×10^{-14}	0.19	Knispel and Petch [10]
ND_3^+ rotation	1.6×10^{-14}	0.20	Howell and Schmidt [11]
NH_2^+ rotation	2.2×10^{-14}	0.43	Knispel and Petch
ND_2^+ rotation	2.2×10^{-14}	0.50	Howell and Schmidt
N_2H_5 motion	10^{-13}	0.69	Knispel and Petch
ND_2-ND_3 mixing	1.3×10^{-11}	0.75	Howell and Schmidt

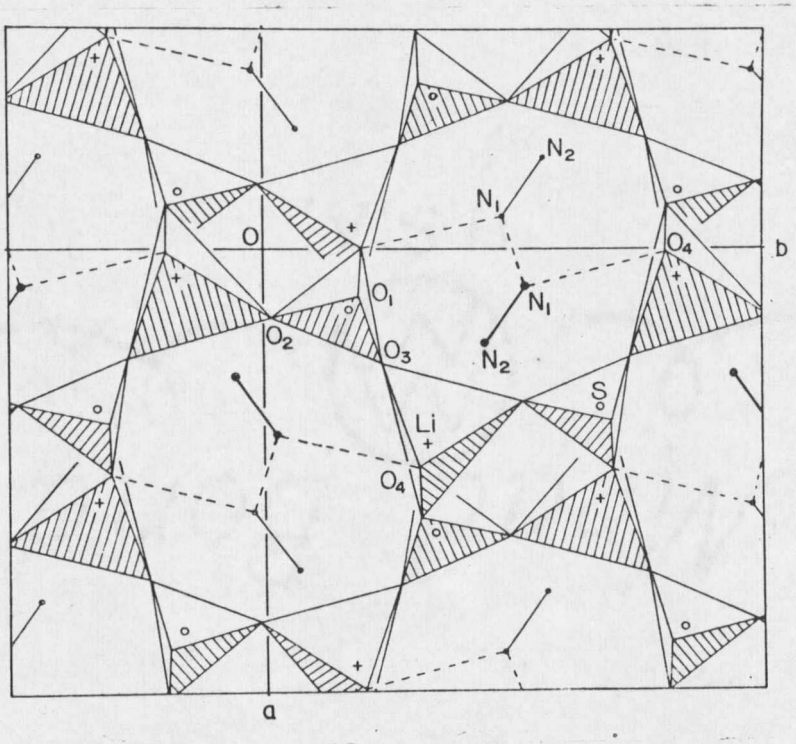

Figure I - 1a LiHzS Projected Down the c-Axis.

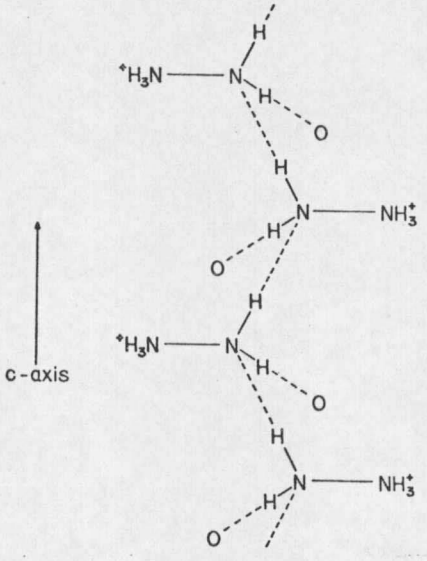

Figure I - 1b View of Hydrazine Chain Along c-Axis.

(N_2H_5+) ions which are composed of NH_2 and NH_3 + groups (Fig. I-1b). The hydrogen locations were found by neutron diffraction studies, while the NMR investigations showed that both the NH_2 and NH_3+ groups undergo hindered rotations. In 1969 Ross, [16] at Brookhaven, did a neutron diffraction study on LiDzS revealing a structure quite similar to LiHzS.

Of particular interest have been the studies of the dielectric properties and electrical conductivity. After Pepinsky's original paper, Vanderkooy, Cuthbert, and Petch[19] measured the conductivity of LiHzS and found a high (about the factor of 200) anisotropy in the conductivity and showed that the high conductivity along the c-axis was protonic in nature. Howell, Schmidt, and Knispel[18] found qualitatively similar behavior for the conductivity in LiDzS.

A surprising feature of the conductivity data is that for temperatures above about 100°C the a- and b- axis conductivities rise more rapidly with increasing temperature, approaching the c-axis value at about the temperature at which the crystal decomposes (Fig. I-2).

Of special interest in this study is the strong possibility that LiHzS and/or LiDzS are not ferroelectric but that the so-called hysteresis loops are the result of a non-linear dielectric. That is, the dielectric constant K is in fact not a constant but a limiting function of applied field.