ANALYSIS OF HYSTERESIS LOOPS IN LiN2H5SO4

V. Schmidt, R. Parker

To cite this version:


HAL Id: jpa-00214971
https://hal.archives-ouvertes.fr/jpa-00214971

Submitted on 1 Jan 1972

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L’archive ouverte pluridisciplinaire HAL, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d’enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.
ANALYSIS OF HYSTERESIS LOOPS IN LiN$_2$H$_5$SO$_4$ (*)

V. H. SCHMIDT †,
Laboratory for Solid State Physics, ETH, Zürich, Switzerland

and

R. S. PARKER
Department of Physics, Montana State University, Bozeman, Montana, U. S. A.

Résumé. — L'observation de boucles d'hystérésis dans des mesures diélectriques de LiN$_2$H$_5$SO$_4$, qui est reconnu comme n'étant pas ferroélectrique, est expliquée par l'intermédiaire de la conductivité protonique pratiquement à une dimension ainsi que par l'extrême influence sur cette conductivité des barrières résultant d'imperfections ou défauts de structure.

Abstract. — The appearance of hysteresis loops in LiN$_2$H$_5$SO$_4$, which has been found not to be ferroelectric, is explained in terms of the nearly one-dimensional protonic conductivity and its extreme sensitivity to barriers caused by impurities or structural defects.

Lithium hydrazinium sulfate (LiN$_2$H$_5$SO$_4$) was first investigated electrically by Pepinsky et al. [1], who observed hysteresis loops for ac fields applied along the orthorhombic c axis. The dc conductivity was found by Vanderkooy, Cuthbert, and Petch [2] to be protonic, and over 200 times greater along c than along a or b. Niizeki and Koizumi [3] were the first to question the ferroelectric nature of LiN$_2$H$_5$SO$_4$. Recent pyroelectric and etching studies [4], [5] provide direct evidence that this crystal is not ferroelectric.

The dielectric susceptibility becomes as great as e = 10$^6$ at 200 °C and 10 Hz, varying exponentially with temperature and approximately as (frequency)$^{-1/2}$. This behaviour has been explained [5] qualitatively by a model having high intrinsic conductivity $\sigma_i$ along the channels parallel to c which contain N-H...N-H... chains. These channels are assumed to contain barriers of random heights caused by impurities and lattice defects. For simplicity, uniform spacing 2 q between adjacent barriers is assumed. To account for the small a and b axis conductivities, high barriers between channels are assumed.

In this investigation of hysteresis loops, the model has been simplified by assuming infinite rather than random barriers to flow along the channels. Because no correlation of barrier location in adjacent channels is assumed, dc conduction along c can still occur by means of carrier jumps to adjacent channels. In fact, because the barrier spacing 2 q is much larger than a lattice constant for best agreement with experiment, the predicted c axis conductivity is still much larger than in the other directions.

(*) On sabbatical leave from Montana State University.

The current density within the segment of a given channel lying between two barriers is governed by a conduction and a diffusion term,

$$J = \sigma_i (1 + f) E_1 e^{i\omega t} - \frac{N e D_1 \partial f}{\partial z} = $$

$$= \sigma_i \left[ (1 + f) E_1 e^{i\omega t} - e^{-1} \frac{kT}{\partial z} \right], \quad (1)$$

using $\sigma_i = N e \mu_i$ and the Einstein relation $\mu_i = e D_i / kT$.

Here $f$ is the fractional deviation of the carrier density from its average value $N$, and the subscript $i$ indicates intrinsic values for z(c) axis components. The term $\sigma_i f E_1 e^{i\omega t}$ accounts for the nonlinear behaviour. The continuity equation is

$$\frac{\partial f}{\partial t} = - \frac{\partial J}{\partial z} - \gamma e N f. \quad (2)$$

The last term, which represents diffusion between channels, is proportional to $f$ in the channel in question because the lack of barrier location correlation gives an average value of zero for $f$ in the adjacent channels. This lack of correlation also precludes the build-up of space charge layers, so the applied field can be assumed to be the local field without serious error. Differentiation of eq. (1) and combination with eq. (2) yields a differential equation involving $f$ as the only variable:

$$\frac{\partial^2 f}{\partial z^2} - e (kT)^{-1} E_1 e^{i\omega t} \frac{\partial f}{\partial z} - \gamma D_1^{-1} f - D_1^{-1} \frac{\partial f}{\partial t} = 0. \quad (3)$$
Its solution consists of harmonics $e^{i\omega t}$ multiplied by hyperbolic functions of $z$. For $z = 0$ midway between barriers, symmetry requires that

$$f(z, t + \pi/\omega) = f(-z, t),$$

so odd $n$ corresponds to sinh terms and even $n$ to cosh terms. The general solution is

$$f = \sum_{n=1}^{\infty} f_n e^{i\omega t} = f_{11} \sinh(k_1 z) e^{i\omega t} +$$

$$+ \left[ f_{12} \cosh(k_1 z) + f_{22} \cosh(k_2 z) \right] e^{2i\omega t} + ...$$

(4)

Here $f_0 = 0$ because of the boundary condition that $J(\pm q) = 0$ which results from the infinite barriers assumed to exist in the channels.

All terms in eq. (3) with the same $m$ and the same power of $e^{i\omega t}$ ($n - 1$ for second term, $n$ for others) must sum to zero. For $m = n$ in the other terms, the second term does not contribute because $m < n$ in eq. (4). Then eq. (3) has the common factor $f_{mm}$ in the three remaining terms, and yields

$$k_n = \left( \frac{n + \pi \omega}{\nu} \right)^{1/2}.$$  

(5)

For $f_{mm}$ ($m < n$) in the other terms, the second has $f_{m,n-1}$ and eq. (3) gives a recursion relation between $f_{mm}$ and $f_{m,n-1}$ which leads to

$$f_{mm} = \left( \frac{-\mu_1 E_1 k_n}{i\omega} \right)^{n-m} f_{m,n-1}.$$  

(6)

With the aid of eq. (6) it is possible to write eq. (4) in the more compact form

$$f = f_{11} e^{i\omega t} \sinh \left[ k_1 z - \frac{\mu_1 E_1 k_1}{i\omega} \right] +$$

$$+ f_{22} e^{2i\omega t} \cosh \left[ k_2 z - \frac{\mu_1 E_1 k_2}{i\omega} \right] + ...$$

(7)

It is now helpful to introduce the dimensionless variables $y = z/q$, $b_n = k_n q$, $u = -\mu_1 E_1/q\omega$, and $r_n = b_n u$. Then using eq. (6), eq. (4) can be rewritten as

$$f = f_{11} \sinh(b_1 y) e^{i\omega t} + \left[ r_1 f_{11} \cosh(b_1 y) +$$

$$+ f_{22} \cosh(b_2 y) \right] e^{2i\omega t} + \left[ \left( r_2^2/2 \right) f_{11} \sinh(b_1 y) +$$

$$+ r_2 f_{22} \sinh(b_2 y) + f_{33} \sinh(b_3 y) \right] e^{3i\omega t} + ...$$

(8)

The arbitrary constants $f_{mm}$ are found from the boundary condition $J(\pm q) = 0$ in conjunction with eq. (1), by writing $f$ in the form

$$J(\pm q) = \sum_{n=0}^{\infty} J_n(\pm q) e^{i\omega t} = 0$$

and noting that $J_n(\pm q) = 0$ for each $n$. As noted before, the $J_0$ equation yields $f_{00} = 0$. The $J_1$ equation has a special form which gives

$$f_{11} = \frac{-u(b_1^2 - b_1^2)}{b_1} \cosh(b_1)$$

(9)

For $n \geq 2$ the condition $J_n(\pm q) = 0$ yields

$$u \frac{i\omega q^2}{D_i} f_{n-1}(\pm 1) + \left( \frac{\partial f_n}{\partial y} \right)_{y=\pm 1} = 0,$$

(10)

from which the following coefficients are obtained:

$$f_{22} = r_1 r_2 \frac{\tanh(b_1)}{(1 - iy/\omega)} \sinh(b_2);$$

$$f_{33} = r_1 r_3 \left( \frac{r_1^2 - r_2^2 \tanh(b_1)}{(1 - iy/\omega)} \right) \cosh(b_3) \times$$

$$\frac{1}{(1 - iy/\omega) \cosh(b_3)}.$$  

(12)

In obtaining hysteresis loops the voltage $E_1 e^{i\omega t}$ applied across the crystal of thickness $w$ is also applied to the horizontal input of an oscilloscope. The vertical input measures the voltage $V$ across a capacitor in series with the crystal. All individual channel segments have the same average current $J(t)$ in this model, so

$$f_{mm} = f_{mn} \left( \frac{-\mu_1 E_1 k_n}{i\omega} \right)^{n-m} f_{m,n-1},$$

(6)

which leads to

$$f_{mm} = (-\pi E_1 km) n-m-1^{n-m} \frac{i\omega}{\pi} \left( \frac{\mu_1 E_1 k_m}{i\omega} \right)^{n-m} f_{m,n-1}.$$  

(13)

The voltage $V$ can be written as a series

$$V_1 e^{i\omega t} + V_3 e^{3i\omega t} + ...$$

as the even harmonics drop out. The coefficients are

$$V_1 = \frac{A_1}{2qC} \int \int J dz \ dt$$

$$= \frac{A_1}{2qC} \int \left[ \sigma_1 E_1 e^{i\omega t} \left( 2 q + \left( \frac{f_{11}}{2} \right) f dz \right) -$$

$$- \frac{kT}{e} \left[ f(q, t) - f(-q, t) \right] \right] \ dt.$$  

(13)

The voltage $V$ can be written as a series

$$V_1 e^{i\omega t} + V_3 e^{3i\omega t} + ...$$

as the even harmonics drop out. The coefficients are

$$V_1 = \frac{A_1}{2qC} \int \int J dz \ dt$$

$$= \frac{A_1}{2qC} \int \left[ \sigma_1 E_1 e^{i\omega t} \left( 2 q + \left( \frac{f_{11}}{2} \right) f dz \right) -$$

$$- \frac{kT}{e} \left[ f(q, t) - f(-q, t) \right] \right] \ dt.$$  

(13)

The voltage $V$ can be written as a series

$$V_1 e^{i\omega t} + V_3 e^{3i\omega t} + ...$$

as the even harmonics drop out. The coefficients are

$$V_1 = \frac{A_1}{2qC} \int \int J dz \ dt$$

$$= \frac{A_1}{2qC} \int \left[ \sigma_1 E_1 e^{i\omega t} \left( 2 q + \left( \frac{f_{11}}{2} \right) f dz \right) -$$

$$- \frac{kT}{e} \left[ f(q, t) - f(-q, t) \right] \right] \ dt.$$  

(13)

The voltage $V$ can be written as a series

$$V_1 e^{i\omega t} + V_3 e^{3i\omega t} + ...$$

as the even harmonics drop out. The coefficients are

$$V_1 = \frac{A_1}{2qC} \int \int J dz \ dt$$

$$= \frac{A_1}{2qC} \int \left[ \sigma_1 E_1 e^{i\omega t} \left( 2 q + \left( \frac{f_{11}}{2} \right) f dz \right) -$$

$$- \frac{kT}{e} \left[ f(q, t) - f(-q, t) \right] \right] \ dt.$$  

(13)
ANALYSIS OF HYSTERESIS LOOPS IN LiN\textsubscript{2}H\textsubscript{5}SO\textsubscript{4} giving a ratio

\[
\frac{V_3}{V_1} = -\frac{1}{45} \frac{\gamma + 3i\omega \left( eE_s q / kT \right)^2}{\gamma + i\omega}.
\] (18)

The hysteresis loop shapes calculated from eq. (16) and (17) for \( \tan^{-1}(\gamma/\omega) = 30^\circ \) are shown in figure 1.

**HYSTERESIS LOOPS IN LiN\textsubscript{2}H\textsubscript{5}SO\textsubscript{4}**

**MEASURED**

**CALCULATED**

\( \omega \)** AND **3\( \omega \)** **TERMS ONLY**

\[ eE_s q = kT \]

\[ eE_s q = 2kT \]

\[ eE_s q = 3kT \]

**FIG. 1.** — Comparison of experimental and calculated hysteresis loops. Measurements were made at 25 Hz and 0 °C.

for three values of the saturation parameter \( eE_s q/kT \), and compared with traces obtained experimentally from single crystals with silver paint electrodes. The calculated curves presumably would have a more conventional shape at high \( E_s \) if the higher harmonics were included.

The loops calculated from these equations have the correct shape only for values of \( \tan(\gamma/\omega) \) near unity. This restricts the loops to a narrow frequency range, whereas experimentally the loops are observable over a range exceeding 10 Hz to 1 kHz. But \( \tan(\gamma/\omega) \) is the dielectric loss tangent for this model, whereas a model with random barrier heights predicts loss tangent near unity over a very wide frequency range as observed experimentally [5]. Accordingly, the predicted narrow frequency range for properly shaped loops results from the assumption of uniform (infinite) barrier heights.

We conclude that the existence of hysteresis loops in LiN\textsubscript{2}H\textsubscript{5}SO\textsubscript{4} is predicted by essentially the same model of partially blocked nearly one-dimensional conduction which accounts for the unusual dielectric susceptibility. Also in other substances the appearance of hysteresis loops should not be considered as proof of ferroelectricity, particularly if nearly one-dimensional conductivity is present.

**Acknowledgments.** — The authors wish to thank Dr. F. L. Howell who grew the crystals. One of us (V. H. S.) wishes to thank the personnel at the E. T. H. for their hospitality during his stay.

**References**


