Internal bias effects on pyroelectric measurements near the Curie temperature in triglycine sulphate
A. Shaulov and M. Simhony

Citation: J. Appl. Phys. 47, 1 (1976); doi: 10.1063/1.322344
View online: http://dx.doi.org/10.1063/1.322344
View Table of Contents: http://jap.aip.org/resource/1/JAPIAU/v47/i1
Published by the American Institute of Physics.

Related Articles
Electro-caloric effect in 0.45BaZr0.2Ti0.8O3-0.55Ba0.7Ca0.3TiO3 single crystal
Appl. Phys. Lett. 102, 082902 (2013)

Interferometric measurement of the pyroelectric coefficient in lithium niobate
J. Appl. Phys. 113, 043101 (2013)

Dielectric and enhanced pyroelectric properties of (Pb0.325Sr0.675)TiO3 ceramics under direct current bias field

The study of dielectric, pyroelectric and piezoelectric properties on hot pressed PZT-PMN systems
AIP Advances 2, 042170 (2012)

Contribution of an extrinsic mechanism for the electrical polarization in BiMn2O5 ceramics
AIP Advances 2, 042165 (2012)

Additional information on J. Appl. Phys.
Journal Homepage: http://jap.aip.org/
Journal Information: http://jap.aip.org/about/about_the_journal
Top downloads: http://jap.aip.org/features/most_downloaded
Information for Authors: http://jap.aip.org/authors
Internal bias effects on pyroelectric measurements near the Curie temperature in triglycine sulphate

A. Shaulov

Physics Department, Ben-Gurion University, Beer-Sheva, Israel

M. Simhon

The Racah Institute of Physics, Hebrew University, Jerusalem, Israel

(Rceived 9 April 1975; in final form 2 June 1975)

Simultaneous measurements of the pyroelectric (PE) coefficient $\lambda$ and permittivity $\epsilon$ from the PE voltage responses to step infrared radiation signals in triglycine sulphate (TGS) are reported as functions of temperature in both the ferroelectric and paraelectric phases. It is shown that the observed lowering and widening of the peaks of $\lambda$ and $\epsilon$, the appearance of a PE effect in the paraelectric phase, and the shift of the $\epsilon$ peak to temperatures above $T_c$ can be explained by the existence of an internal bias field $E_b$. The values of $E_b$ calculated to fit the experimental results vary in different TGS samples from 30 to 150 V/cm.

PACS numbers: 77.70., 77.20.

I. INTRODUCTION

The appearance of the pyroelectric (PE) effect above the Curie temperature $T_c$ in triglycine sulphate (TGS) was first reported by Chynoweth and ascribed to space-charge polarization in the crystals. It was also observed in TGS that the permittivity $\epsilon$ reaches maximum at a temperature $T_{\text{em}}$ which is 0.2–0.5 °C higher than the temperature $T_{\text{wm}}$, at which the PE coefficient $\lambda$ has a maximum. Here we report simultaneous measurements of $\lambda$ and $\epsilon$ from PE voltage responses to step infrared radiation signals in TGS around $T_c$. The irregularities in the behavior of $\lambda$ and $\epsilon$ are explained by the influence of an internal bias, based on the thermodynamic theory of a second-order ferroelectric phase transition.

II. CALCULATION OF $\lambda$ AND $\epsilon$

Consider a ferroelectric crystal with a second-order phase transition to which an electric bias field $E_b$ is applied parallel to the polarization vector $P$. For temperatures $T$ close to $T_c$ and in the absence of external pressure, the thermodynamic theory yields

$$ [(T - T_c)/\epsilon \gamma] P + \eta P^3 - E_b = 0, \quad (1) $$

where $\epsilon = 8.85 \times 10^{-12}$ F/m, $\gamma$ is the Curie-Weiss coefficient, and $\eta$ is a constant parameter. The PE coefficient $\lambda = |dP/dT|$ is, therefore,

$$ \lambda = P/(T - T_c + 3\epsilon \gamma P^2), \quad (2) $$

and for the relative dielectric constant $\epsilon = \epsilon_0(dP/dE_b)$, one obtains

$$ \epsilon = \gamma/(T - T_c + 3\epsilon \gamma P^2). \quad (3) $$

Taking $d\lambda/dT$ it was shown that $\lambda$ has a maximum value $\lambda_m$,

$$ \lambda_m = (3\epsilon_0 \gamma^{2/3} E_b^{1/3})^{-1}, \quad (4) $$

at $T = T_{\text{em}}$, i.e., $T_{\text{wm}} = T_{\text{cm}}$ independent of bias. Unlike this, $\epsilon$ has a maximum value $\epsilon_\text{m}$ (assuming $3/2^{1/3} = 2.4$)

$$ \epsilon = (2\epsilon_0 \gamma^{1/3} E_b^{2/3})^{-1}, \quad (5) $$

at a temperature $T_{\text{em}}$ higher than $T_c$.

$$ T_{\text{em}} - T_c = 1.2\epsilon_0 \gamma^{1/3} E_b^{2/3}. \quad (6) $$

Thus, the bias field shifts $T_{\text{em}}$ away from $T_{\text{wm}} - T_c$ by an amount proportional to $E_b^{2/3}$.

Under the condition

$$ E_b \ll (|T - T_c|/\epsilon_0 \gamma^{1/3})^{3/2}, \quad (7) $$

Eq. (1) has the linear solutions

$$ P = P_0(T) + \epsilon_0\gamma E_b/(T - T_c), \quad T > T_c, \quad (8) $$

while always $P(T = T_c) = (E_b/\gamma)^{1/3}$ [Eq. (1)]. Here $P_0 = P(E_b = 0)$ is the spontaneous polarization,

$$ |P_s| = [(T_c - T)/\epsilon_0 \gamma]^{1/3}, \quad T < T_c \quad (9) $$

$$ |P_s| = 0, \quad T > T_c. \quad (10) $$

With Eqs. (7) and (8) one has

$$ \lambda = \lambda_0 - \epsilon_0\gamma E_b/(T - T_c)^2, \quad T > T_c, \quad (11) $$

where

$$ \lambda_0 = \left| \frac{dP_0}{dT} \right| = \frac{1}{2} \left( \frac{\epsilon_0 \gamma}{T_c - T} \right)^{1/2}. \quad (12) $$

Thus, below $T_{\text{em}}$ far enough to satisfy Eq. (7), $\lambda$ rises with $T$ almost as $\lambda_0$, i.e., proportional to $(T_c - T)^{-1/2}$. Above $T_{\text{em}}$, far enough again to fulfill Eq. (7), $\lambda$ decreases as $(T - T_c)^{-2}$. At $T = T_c$, the rising and falling branches of $\lambda$ meet having the value $\lambda_m$. With Eqs. (7) and (8) one also has

$$ \epsilon = \gamma/(T - T_c), \quad T < T_c \quad (13) $$

$$ \epsilon = \gamma/(T - T_c), \quad T > T_c, \quad (14) $$

i.e., $\epsilon$ is independent of $E_b$ and obeys the Curie-Weiss law. Reversing Eq. (7) one finds that the linear approximation applies for temperatures

$$ |T - T_c| > \epsilon_0 \gamma^{1/3} E_b^{2/3}. \quad (15) $$

Copyright © 1976 American Institute of Physics
Comparison with Eq. (6) shows that in the paraelectric phase the linear approximation [Eqs. (8), (10), (12)] applies for temperatures above $T_{m}$. 

In TGS one has $\gamma = 3200 \, \text{K}$, $\eta = 6.5 \times 10^{11} \, \text{Jm}^3/\text{C}^4$, and $T_c = 49.5 \, \text{C}$, so that, with $E_b$ in $\text{V/cm}$,

$$P(T=T_c) = 0.54 E_b^{1/3}, \ \mu\text{C/cm}^2$$  

$$\lambda_m = 3.4 E_b^{1/3}, \ \mu\text{C/cm}^2 \text{deg}$$  

$$\epsilon_m = 2.5 \times 10^5 E_b^{2/3}, \ \text{K}$$  

$$T_m - T_{m_e} = 6.3 \times 10^{-3} E_b^{3/2}, \ \text{K}$$

These parameters are plotted in Fig. 1 against $E_b$. The linear approximation applies for $E_b \ll 2600 \left| T_c - T \right|^{3/2} \text{V/cm}$ or, in the paraelectric phase, for temperatures $T - T_c$ lying above the $T_{m_e} - T_c$ line [Eq. (13)]. The derived equations and parameter values were used to compute $P$, $\lambda$, and $\epsilon$ in TGS under bias fields of 0, 50, 250, and 1000 $\text{V/cm}$. Results are presented graphically as functions of $T-T_c$ in Fig. 2.

III. EXPERIMENTAL TECHNIQUE

Measurements were carried out on six samples of single-crystalline TGS with major faces oriented perpendicular to the PE axis and provided with IR transparent electrodes (evaporated InSb). The thickness $L$ of the samples was 15–70 $\mu\text{m}$, and their electroded radiation-receiving area $A$ was 0.5–4 $\text{mm}^2$. Attached to the electrodes were 8–$\mu\text{m}$ thin leads of stainless steel which also served as suspenders. The samples were placed in a small oven with a CdS window. The oven was thermometer controlled with temperature stability better than 0.05 $\text{C}$. The temperature of the sample was measured to $\pm 0.1 \, \text{C}$ with a calibrated thermocouple attached very close to the rear electrode. The whole mount was held in a vacuum-tight (up to $10^{-6}$ Torr) cryostat with a KBr window, in which the sample could be poled in a field up to $10^5 \, \text{V/cm}$.
The radiation source was a 500 °K blackbody with a shutter fast enough to provide step signals. The measuring circuit consisted of interchangeable load resistors $R_L$ ($10^5-10^7 \Omega$) connected parallel to the sample and to a FET source-follower circuit, as shown in Fig. 3(a). $R_L$ was small to keep the measured electronic time constant $\tau_e = R_L C$ much smaller than the thermal time constant $\tau_T$ of the sample, which was 0.5-3 sec. A larger value of $R_L$ may also introduce an additional bias due to the backward current through the FET. For example, a $10^{-14}$-A flow on $R_L = 10^{10} \Omega$ would yield ~50 V/cm on our samples. The PE response transients were displayed on a Tektronix RM 564 storage CRO with a 3A9 amplifier of usable sensitivity 50 µV/cm.

A schematic PE voltage response is shown in Fig. 3(b). The measured ratio $\delta = \tau_e / \tau_T$ is 0.2. The measured parameters of the response are the initial slope $k$, the peak value $V_p$, the rise time $t_r = \tau_T$, and the fall time $t_f = \tau_T$. From these parameters $\lambda$ and $\epsilon$ are calculated with the use of relations

$$\epsilon = \left( \frac{L}{\epsilon_0 AR_L} \right) \tau_T, \quad \lambda = \left( \frac{c L}{FAR_L} \right) V_p, \quad \text{and} \quad \frac{\lambda}{c_0 \epsilon} = \frac{k}{F},$$

(14)

where $F$ is the radiation flux absorbed in the sample and $c$ is the volume specific heat. The measurement is valid under the small-signal condition.

**TABLE I. Data for Fig. 5.**

<table>
<thead>
<tr>
<th>Line</th>
<th>I</th>
<th>II</th>
<th>III</th>
</tr>
</thead>
<tbody>
<tr>
<td>Internal bias (V/cm)</td>
<td>30</td>
<td>40</td>
<td>150</td>
</tr>
<tr>
<td>Sample</td>
<td>T-18</td>
<td>T-20</td>
<td>Z-3</td>
</tr>
<tr>
<td>Thickness (µm)</td>
<td>60</td>
<td>20</td>
<td>40</td>
</tr>
<tr>
<td>Area (mm²)</td>
<td>4</td>
<td>3.3</td>
<td>2</td>
</tr>
<tr>
<td>$\tau_T$ (sec)</td>
<td>2.4</td>
<td>1.5</td>
<td>2.2</td>
</tr>
<tr>
<td>$\Delta T_s$ (°K)</td>
<td>0.07</td>
<td>0.12</td>
<td>0.1</td>
</tr>
</tbody>
</table>

**FIG. 3.** (a) Measuring circuit. (b) Schematic PE voltage response to a step signal for $\theta = 0.2$; $\Delta T$ is the exponential temperature rise of the sample during the signal to the saturation value $T_s$, with time constant $\tau_T$.

**FIG. 4.** Experimental values of $\lambda$ (circles) and $\epsilon$ (triangles) as function of temperature. The theoretical $\lambda$ and $\epsilon$ curves are computed for $E_B = 150$ V/cm.

$$\theta \Delta T_s \ll |T_0 - T|,$$

(15)

where $\Delta T_s$ is the saturation value of the exponential temperature rise of the sample during the radiation signal, as shown by the lower curve of Fig. 3. The values of $c$ in TGS are taken from the literature (in the interval under consideration $c$ varies between 2.2

**FIG. 5.** Experimental $\lambda^{1/2}$ values in three TGS samples as functions of temperature in the paraelectric phase. The straight $\lambda^{1/2}$ lines are calculated with $E_B = 30$, 40, and 150 V/cm. Other details are shown in Table I.
FIG. 6. Oscillogram of the PE voltage response to a step ir signal (upper trace) and of the response to a following step dark signal (lower trace) in a TGS sample in the paraelectric phase. T=49°C, R = 10^5 Q; vertically 5 mV/div, horizontally 0.5 sec/div.

and 2.6 J/cm³ deg). However, c can also be calculated using

\[ c = \frac{F}{L} \left( \frac{\tau_p}{\Delta T_e} \right), \]

The response to the light signal is seen to decay faster. Obviously, due to the temperature rise during the signal \( \lambda \) decreases helping to reduce the height of the response. During the dark signal, due to the cooling of the sample, \( \lambda \) increases delaying the fall of the response.

### V. DISCUSSION AND CONCLUSIONS

Based on the thermodynamic theory of a second-order ferroelectric phase transition\(^5,^{10}\) and on the works in Colemanite crystals,\(^4\) we have calculated the effects of an electric bias field on the polarization, pyroelectric coefficient, and permittivity in TGS around the Curie temperature in the ferroelectric and paraelectric phases. Because of the bias, the polarization does not vanish at the Curie point, but continues to higher temperatures. The pyroelectric coefficient reaches a lower maximum at \( T = T_c \), but does not vanish thereafter and is a continuous function of \( T \) in the paraelectric phase. The dielectric constant, too, has a lower maximum, occurring above \( T_c \), the further the stronger the field. Because under bias the peaks of \( \lambda \) and \( \epsilon \) become lower and wider, the transition between the paraelectric and ferroelectric phases is obscured. All these effects were observed in our measurement of \( \lambda \) and \( \epsilon \) from PE voltage responses to step ir radiation signals in TGS crystals without external bias, and we have shown that they can be adequately explained by the action of internal bias fields. The values of the internal bias calculated to fit the experimental results vary in different samples from 30 to 150 V/cm, and could change after heating the samples above \( T_c \) and recooling. Other measurements of \( E_g \) out of hysteresis loops\(^6\) in TGS have yielded similar values of \(-40 \text{ V/cm}\), while alaninedoped samples had internal bias fields of \(-10^6 \text{ V/cm}\).

The correction of \( P \) and \( \lambda \) above \( T_c \) was previously observed\(^4\) in Colemanite and GASH crystals and explained by an internal bias causing a shift of the hysteresis loop.\(^4\) Similarly, the appearance of \( \epsilon \) above \( T_c \) and the deviation of \( \epsilon \) from the Curie-Weiss law in Colemanite were explained, too, by an internal bias.\(^5,^6\) Our measurements from PE responses yield simultaneously the bias effects on both \( \lambda \) and \( \epsilon \), thus also the shift between their maxima. The PE measurements do not require the application of external fields and so affect the internal bias much less than hysteresis loop measurements, especially around \( T_c \). It has been suggested\(^4\) that the internal bias depends on the purity of the samples and that it should not exist in perfect TGS crystals. Such an assumption is reasonable in view of our experience; however, a definite answer cannot be given on the basis of this work, requiring samples of sufficiently more grades of perfection and a deep insight into the history of their growth, thermal and electrical treatment, and an account of possible diffusion of electrode material.
