A Low Temperature Investigation of Possible Domain Wall or Pseudo-Spin Wave Contributions to the Specific Heat of Ferroelectric Materials

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Abstract

Ferroelectric crystals show an unexpected $T^{3/2}$ term in the specific heat. An experiment is discussed, as well as background information on ferroelectrics and specific heats, in which the thermal expansion coefficient is measured in the presence of electric fields of various strengths.

I. Introduction

The experimentally measured specific heats of ferroelectric crystals at low temperatures have yielded some unexpected contributions due to temperature.

A ferroelectric crystal is one which exhibits a temperature dependent hysteresis loop on a graph of the electric field vs. the dipole moment. In a certain temperature region - below the "Curie point" the curve will trace out the loop shown below:

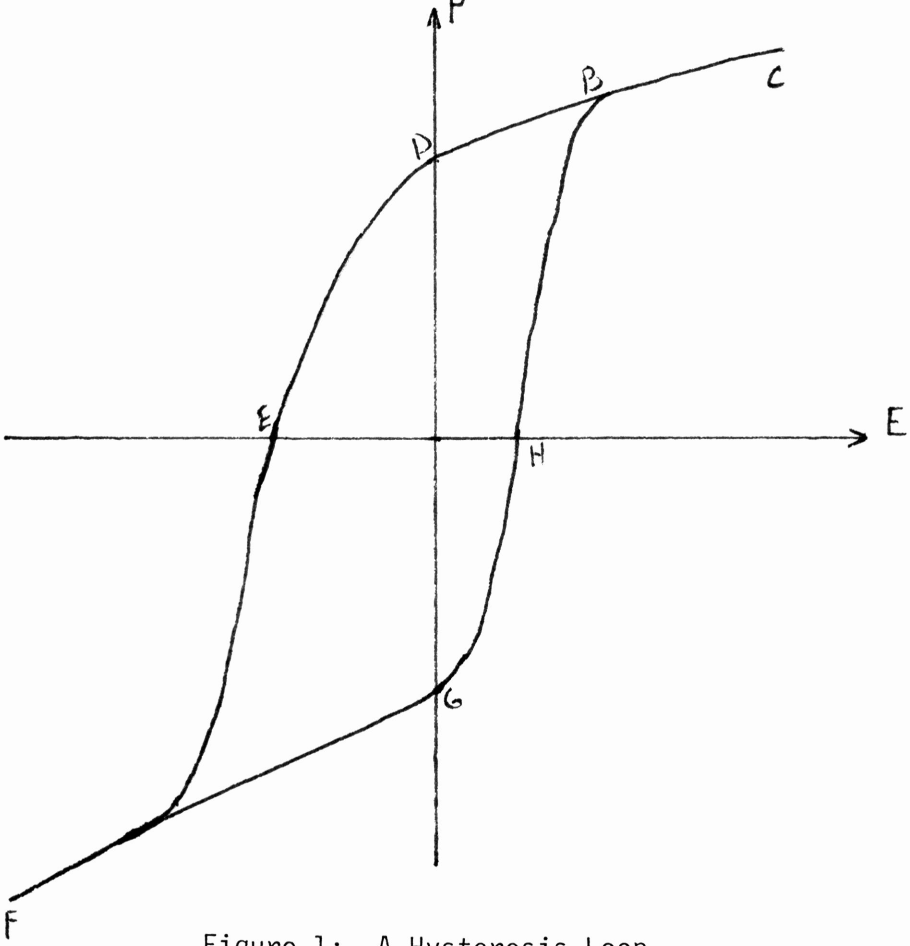

Figure 1: A Hysteresis Loop

As the electric field strength is varied along the path FGHC, the crystal goes from a saturated state (all the dipoles oriented in the direction of the field) to one in which the net dipole moment is zero, to a saturation state pointing in the opposite direction. A careful decrease of the field will then return the crystal to state F via path BDEF.

In 1922, Debye developed a theoretical derivation of the specific heat (classically thought to be a temperature independent parameter), which dependend upon the third power of the temperature. His equation suffered somewhat under laboratory verification because it was virtually impossible at that time to take into account certain conditions existing in the real world. It has therefore become somewhat modified over the years, but the fundamental dependence upon the cube of the temperature still remains.

However, about one year ago, Dr. W. N. Lawless, of the Corning Glass Works Research Laboratory presented a paper in which he obtained some anomalies in the experimentally measured specific heats of the ferroelectric substances triglycine sulfate (TGS), potassium dihydrogen phosphate (KDP), $BaTiO_3$, and $LiNbO_3$ in the region of 2°-37° K. He also obtained numerous data about the specific heats of several paraelectrics (PbF_2, $KTaO_3$, TlCl, TlBr, TlI) and antiferroelectrics ($Pb(Zr_{0.95}Ti_{0.05})O_3$ and $Pb_2Nb_2O_7$) in this temperature region; the results of this data were not, however, revolutionary enough to cause the revision of existing theories. These substances have not previously been studied at temperatures below the boiling point of nitrogen (77° K), so Dr. Lawless' work represents a substantial increase in our knowledge of these materials in this region. In the case of ferroelectric materials, he not only found the specific heats of the materials in question (both displacive and hydrogen bonded ferroelectrics), but also discovered a previously unknown component of the specific heat. Upon analysis, this term was found to depend upon the 3/2 power of the temperature. Dr. Lawless hypothesized two possible mechanisms for this term - a pseudo-spin wave mechanism similar to that which generates a $T^{3/2}$ term in ferromagnetic crystals, or possibly domain wall activity inside the crystals.

II. The Experimental Apparatus

My method of approach has been to study the linear thermal expansion of the crystals. The coefficient of thermal expansion can be related to the specific heat by statistical thermodynamics. The domain wall activity will be varied by the application of electric fields across the crystal; this will similarly affect any dependence of the thermal expansion on domain activity.

This parameter can be measured by the use of a capacitance bridge since capacitance is inversely proportional to the distance between plates. The experimental setup is pictured in the following two figures:

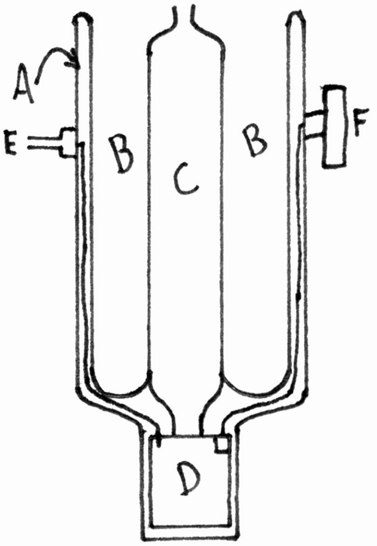

Figure 2: Dewar Cross Section

The dewar (Sulfrian Cryogenics model S-1004) consists of an evaporated jacket (area A) surrounding a liquid nitrogen bath (area B) and an evacuated area (D) for performance of the experiment, which in turn surrounds area C, containing liquid helium. Area C extends downward in a "cold finger" which reaches down to the experimental setup in area D. A pipe extends from E to area D for the purpose of carrying the necessary wiring. In addition, the dewar is equipped with a constant volume gas thermometer (F) which operates according to the ideal gas law, $T = P(\frac{V}{NR})$. It consists of a small metal bulb containing helium which is essentially a pressure gauge. The temperature can be calculated easily, being a linear multiple of the pressure.

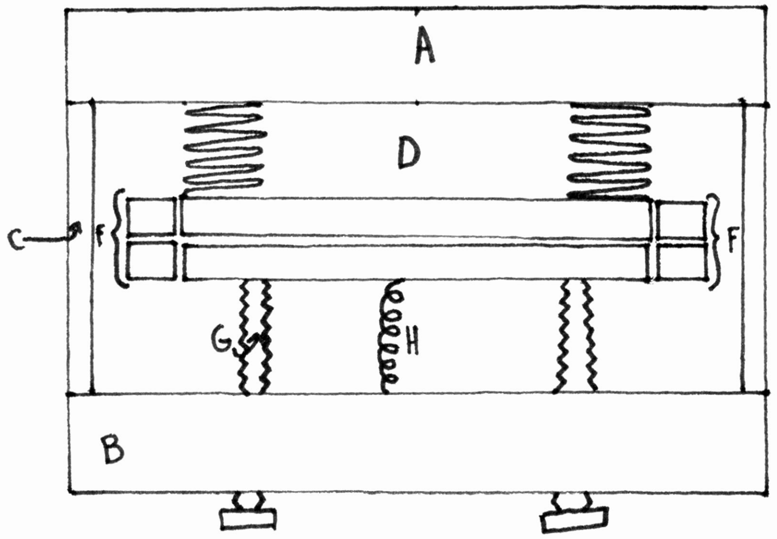

Figure 3: Cross Section of the Experimental Device

A&B are the top and bottom, respectively, of the setup; A provides a thermal link between the crystal, which is located directly underneath it, and the liquid helium just above it. B holds in place the two adjusting screws (G) which set the height of the reference capacitor plate. They are both 1.8" in diameter, .25" thick and constructed of stainless steel. C is one of the three posts connecting A&B, .75" long, .08" in diameter and made of beryllium copper. D is a copper bellow, .25" long, with an inner diameter of .8". Its purpose is to hold the crystal tight against A and the mobile capacitor plate. F is the capacitor and guard rings. The plates are roughly 1.19" in diameter by .1" thick. They are separated from the guard rings by a .004" electrically insulated gap. All four items are constructed of beryllium copper. The guard rings form a separate capacitor surrounding the main measuring capacitor. The electric lines of force between two capacitor plates tend to bulge outward at the edge; this condition, if uncorrected, would cause incorrect capacitor readings. This can be remedied by another capacitor around the edges of the important one, electrically insulated from it. The lines of force at the outer edge of the measurement capacitor and the inner edge of the guard rings will repel and thus keep each other perpendicular to their respective plates. A constant electric field will be established across the body of the crystal by gold plating it around the sides. Not shown in figure 3 are the wires of the capacitors and the thermometer and the heater wire. The capacitance bridge is an Impedance Bridge model 290-B from Electro Scientific Industries with a sensitivity of .01 picofarads. H is a spring which holds the fixed capacitor place down on the adjusting screws.

The sensitivity of the equipment can be determined in the following manner:

$$C = \frac{\varepsilon_o A}{D} \qquad \Delta C = \frac{\varepsilon_o A}{D_f} - \frac{\varepsilon_o A}{D_i} = \varepsilon_o A\left(\frac{1}{D_f} - \frac{1}{D_i}\right)$$

$\frac{1}{D_F} = \frac{1}{D_i + \Delta D} = \frac{1}{D_i}\left(1 - \frac{\Delta D}{D_i} - \frac{\Delta D^2}{D_i^2} \cdots\right)$. Dropping all but the first two terms, $\frac{1}{D_F} = \frac{1}{D_i} - \frac{\Delta D}{D_i^2}$

$\Delta C = \varepsilon_o A\left(\frac{1}{D_i} - \frac{\Delta D}{D_i^2} - \frac{1}{D_i}\right) = -\varepsilon_o A\left(\frac{\Delta D}{D_i^2}\right)$ or, conversely

$$\Delta D = \frac{(\Delta C)(D_i^2)}{\varepsilon_o A}$$

where C is the capacitance, D is the distance between plates, A is the plate area, and ε_0 is the permittivity constant, 8.85×10^{-12} farads/meter. With a capacitance sensitivity = .01 picofarads, D_i = .004" and A = 1.1 square inches, ΔD can be measured in integral multiples of 1.6×10^{-8}m.

III. Experimental Procedure

The perceived procedure is to take a prepared crystal and gold plate it on top and bottom, attaching leads to the plating so that it can establish a constant electric field throughout the crystal. The crystal will be placed inside the bellows. The crystal temperature will be regulated by a heater wire coiled around the sample. Increasing temperature will result in an increasing length and will register as decreasing capacitance. This experiment will be conducted in a temperature range of 1°-20° K for each of three different electric fields on the crystal. The materials chosen for this experiment are those which Dr. Lawless used in his work, TGS, KDP, $BaTiO_3$, and $LiNbO_3$. I will also use $LiTaO_3$, which he did not use, and also PbF_2 (a paraelectric) for reference purposes.

IV. Results

At this time, I have succeeded in sealing the dewar against leaks, and in designing the desired equipment. I have received a specimen of TGS and am presently in contact with persons around the country who can supply other samples. Also , the Physics Department Machine Shop is just now completing some of the parts needed for the capacitance expansometer.

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