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REPORT ON PHASE 1A
of
DEMONSTRATION OF SCIENTIFIC
AND ECONOMIC FEASIBILITY OF A
SOLID-STATE HEAT ENGINE

MASTER

DOE Contract No. ER-78-C-03-1736

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Washington, D.C. 20545

on
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Prepared By
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I INTRODUCTION

The main goal of Phase 1A was to demonstrate the thermal-electrical cycle projected in the original proposal. The demonstration was to be in the form of a measured temperature-entropy (T-S) curve executed in the power production (clockwise) direction. (This would be like Figure 10 in the proposal though we were not constrained to use that particular material or temperature range.) If the measured T-S diagram represented a sufficiently large single stage efficiency, it would constitute a partial "proof of concept" for one stage of the new heat engine. The concept presented in the proposal improved upon earlier proposals by others in that our projected cycle efficiency was much greater than was thought to be possible with even the best dielectrics and optimum operating conditions¹. The challenge we undertook with this contract was to demonstrate in the laboratory with real materials, an efficiency greater than the previous theoretical upper limit for ideal materials. This challenge proved difficult -- it took us two and one-half months longer than expected -- but it was accomplished! Figure 1 shows a cross-plot of temperature versus entropy obtained by sampling 2400 cycles of the engine operation. The efficiency of this cycle is nine times the upper limit theorized for ideal

conditions! Yet, one may feel that this is a Pyrrhic victory since, in spite of the improvement, the efficiency is only 0.23%, and that without allowing for hysteresis and other system losses. The point, of course, is that the observed cycle partially validated the new method of forecasting cycle performance which was presented in the proposal. The details and extent of validation are discussed in latter sections of this report. We simply note here that it is this approach (tested today for a tiny, impure sample too thick and too low in polarization density) that also forecasts high efficiency, high power density devices with realizable materials tailored in doping.

The following sections of this report are organized in accordance with the major tasks of this program: Section II reports on measurements of material parameters relevant to dielectric power conversion, hysteresis reversal time, Curie temperature, Devonshire coefficients and resistivities. Section III reports on the engine cycle tests, and Section IV analyzes performance versus predictions, makes engineering and economic projections based upon these results and identifies engineering and materials problems.

FIGURE 1: TEMPERATURE vs ENTROPY RELATION MEASURED FOR APPROXIMATELY 2400 CONTINUOUS THERMAL CYCLES.

FIGURE 2:

II PARAMETER MEASUREMENTS

2.1 Hysteresis

One of the salient features of the engine described in the proposal is its large power density compared with earlier projected electro-caloric heat engines. This results in part from use of the full polarization-field strength characteristic of ferroelectric materials rather than a restricted region around the remnant polarization. The trade-off involved is efficiency loss due to encountering the hysteresis loop. In order for electrostatic energy stored in the capacitor (plus thermal energy abetting discharge of the capacitor) to force reversal of the dielectric polarization, operating temperature can be only a few degrees below the Curie temperature. It was proposed that the hysteresis loop would be effectively closed by action of the inductor which was part of the engine circuit. The fraction of the loop area remaining was taken as the ratio of the reversal time of the material in a low impedance circuit to the reversal time permitted by the inductive circuit. Since reversal times of microseconds had been reported in the literature, this seemed to indicate that effective closure could be obtained with reversal times constrained to several milliseconds by the inductor. Unfortunately, the ferroelectric samples we were able to obtain had essentially infinite spontaneous reversal times as is indicated by the sloping sides of their hysteresis loops. The problems this presented and their consequences are detailed in Appendix A and discussed in Section IV. Measurements of driven polarization reversal times are presented in Appendix B.

In summary, we find hysteresis loss can be controlled by means of external circuitry but that the extent of this control is limited by impurities (heterogeneous doping) within the samples. This, we feel, represents in itself a significant contribution to the science and applications of ferroelectrics. Hysteresis loss has in the past been an inherent limitation to the use of ferroelectric capacitors in circuits which were sensitive to the degraded Q caused by their dissipation factor. Also, hysteresis heating raises the temperature (we have measured as much as 50°C) of a ferroelectric capacitor; its properties change so much that it is totally unsuitable for some purposes for which low Q as such would not be objectionable. Our present and continuing work may benefit these neighboring areas of technology.

2.2 Curie Temperature

Curie temperature was found to vary widely from sample to sample as shown by Figure 2. This suggests that even within a given sample, elements will have a distribution of Curie temperatures resulting from irregularities in doping. The consequence of a statistical distribution of Curie temperatures would be sloping sided hysteresis loops like those actually observed. From measurements at a variety of temperatures it is possible, as shown in Appendix A, to infer the statistical spread in the distribution of Curie temperatures within a single sample. When this was done for a sample similar to that used in the thermal cycle, Figure 1, it was found that the standard deviation of Curie temperatures was 16°C.

2.3 Devonshire Coefficients

The literature is remarkably sparse when it comes to systematic characterization of Devonshire coefficients. A few excellent papers exist¹, but they are the exception. We therefore have undertaken this work in order to be able to make comparisons between the theoretical and experimental engine thermal cycles. The method we have chosen as simplest and most reliable experimentally is measurement of remnant polarization density (of well poled samples) versus temperature. The experimental arrangement is shown in Figure 3. The temperature of the sample is gradually raised while switches S_1 and S_2 are open. At intervals of a few degrees Celsius switch S_1 is closed for a few seconds charging C with the difference in remnant polarization developed over those few degrees. S_1 is then opened and S_2 is closed so that the deflection on a storage oscilloscope can be seen. S_2 is left closed until the input vertical deflection ceases, indicating that the input resistance of the oscilloscope has discharged C. The initial deflection is recorded adjacent to the temperature at which S_1 had been closed. The screen is then erased and the procedure repeated at higher temperature. Only rising temperature is used in the data run because the polarization switching of regions within the sample are, of course, not reversible. The remnant polarization density of the sample at room temperature is given by the sum of all the charges that are removed from the sample (as the temperature is raised from room temperature to well above the Curie temperature

FIGURE 3
EXPERIMENTAL ARRANGEMENT FOR MEASURING
REMANT POLARIZATION OF FERROELECTRIC CAPACITORS

of any region within the sample) divided by the electrode area of the sample, A. (Charges removed decrease toward zero at high temperatures.) The polarization density, $\sigma(T)$, at any temperature, T, is then computed as the difference between the room temperature polarization density and the sum of all the charges per unit area removed between room temperature and T. The analytical expression for σ is:

$$\sigma(T) = \frac{1}{A} \sum_{i=1}^N \sigma_i(T) A_i, \quad A = \sum_{i=1}^N A_i \quad (1)$$

where $\sigma_i(T)$ is the remnant polarization density of the region characterized by an area A_i and Weiss temperature T_i which is determined by the level of dopant within that region. In order to compare this expression with the measured values of $\sigma(T)$, we took a 10 region equal area model having a normal distribution of T_i 's. We made a least squares fit of 62 measured values of σ to those given by Eq.(1) varying the mean Weiss temperature, the value of the standard deviation of the distribution of Weiss temperatures and the ratios B/γ and C/γ of the Devonshire coefficients. The fit was so close that the r.m.s. error in $\sigma_{\text{measured}} - \sigma_{\text{calculated}}$ over the 62 temperatures was only 0.005 coulombs per square meter which is much smaller than the measured room temperature remnant polarization density of 0.3 coulombs/m². The results were:

$$\begin{aligned} T_0 &= 178^\circ\text{C}, \text{ std. dev. of } T_0 = 16^\circ\text{C}, \\ B/\gamma &= 236.4, C/\gamma = 37530 \text{ (S.I.units)} \end{aligned} \quad (2)$$

The value of $\gamma = \frac{\partial \frac{1}{\epsilon}}{\partial T}$ was measured by a least squares fit

of $1/\epsilon$ to a straight line at high temperatures. The result was:

$$\gamma = 2.9 \times 10^5 \quad (\text{S.I. units}) \quad (3)$$

with a correlation coefficient of 94%.

2.4 Resistivities

For the temperatures at which we have worked, power loss through conduction within our samples has apparently not been a problem. Some examples of resistivity measurements we have made by means of a self-discharge technique are given in Figure 4.

FIGURE 4

ρ v.s. $T^{\circ}\text{C}$

for PSZT, PZT, and BaTiO_3

$\rho \times 10^{-10} \text{ ohm-cm}$

III ENGINE CYCLE TESTS

3.1 Requirements

The requirements for a thermal cycle test include a test system design to accomplish the following:

1. Periodic heating and cooling of a ferroelectric sample material with variable frequencies and delay times
2. Periodic controllable discharging/charging of the ferroelectric sample during and following the heating and cooling cycles
3. A plot of the temperature change as a function of entropy change of the ferroelectric

A considerable amount of development was required to arrive at a system design to accomplish the above requirements. This is particularly true for the instrumentation for measurement of the system phenomena which must be integrated with the design of the system hardware.

3.2 Thermal System

For the first requirement of heating and cooling, several approaches were tested before arriving at the final system now in use. The four design approaches considered were as follows:

- (1) The first concept for pulsing was a rotating disc, or wheel with windows located 180° apart. The heat source was a continuous or pulsing radiant lamp or a dry steam source. The cooling was done by directing a pulsing stream of atomized water vapor at nearly saturated steam conditions. As the windows rotated past the ferroelectric material the heat source alternating with the cooling vapor was pulsed to impinge on the target. This system was never developed for the heat engine thermal cycle test in entirety. However, parts of the design concept are used in the final test system design. Also, the system was used in a modified fashion to calibrate the infrared detector as shown in the photograph of Figure 5. The heat source was an electrically heated cylinder

SHUTTERWHEEL DRIVEN BY A VARIABLE SPEED
ELECTRIC MOTOR TO TEST RESPONSE OF THE I-R
DETECTOR WHEN HEAT IS PRE-SET IN THE FAR
SIDE OF THE CHAMBER.

FIGURE 5

behind the rotating wheel which was controlled at $\sim 101^{\circ}\text{C}$. The baseline temperature for the IR detector was the temperature of the rotating wheel which was controlled by an electrical heater at about 98°C . The temperatures were measured by thermistors. The results indicated that the IR detector response to temperature was about $17\text{ mV}/^{\circ}\text{C}$. Further calibration with the other systems modified this to $15.8\text{ mV}/^{\circ}\text{C}$.

- (1a) The heat source to the ferroelectric planned for the first phase was dry saturated steam at atmospheric pressure. Thus, the ferroelectric sample would receive heat at a surface temperature of 100°C . For a controlled steam heat, an ordinary household aluminum pressure cooker was modified (both Mirromatic and Presto brands were used). The heat source was a laboratory hot plate and the fine temperature control was provided by an electrical heater wrapped around the outer surface of the cooker. An OMEGA temperature controller was used to control temperatures to $\pm 2^{\circ}\text{C}$. The steam pressure from the cooker is used to drive the steam to the ferroelectric target which is mounted in the center of a two-part chamber.
- (1b) The heat sink pulsing system considered was an air nozzle spraying atomized, saturated boiling water for cooling the ferroelectric. For this cooling system, an ordinary artist's air brush (Sears-Roebuck) was proposed. The system was setup and briefly tested using a mechanical cam actuated pulsing drive (see Figure 6).
- (2) The second pulsing system proposed and built was a disc or wobble plate rotated about an axis making an angle with the normal to the plate. The plate was in a cylinder so that it opened and closed input and output ports. A variable speed DC motor was used. The system is shown in Figures 7 (a schematic) and 8 (a photograph). The disc was made of two stainless steel plates and a thin disc of teflon was sandwiched between the plates to provide a rotating seal. The cylinders were first made of clear polycarbonate plastic material, but later changed to aluminum because of surface melting of the teflon seal caused by high

FIGURE 6

VAPOR COOLING SYSTEM
FOR PULSED COOLING OF SOLID-STATE HEAT ENGINE

FIGURE 7

HEAT PULSER SYSTEM No. 2, A PAIR
OF ENCLOSED WOBBLE PLATES

FIGURE 8

MINIATURE SOLENOID VALVES FOR
HEAT PULSER SYSTEM No. 3

FIGURE 9

friction. Two cylinders and discs were used on the same drive shaft, one for a pulsing dry steam heat source and the other for a pulsed cooling saturated water source. A variable phase angle coupling connected the shafts of the two rotating discs. Thus the drive frequency and the phase synchronization of the heating and cooling pulses were completely variable. This system was tested and appeared to be a viable one. However it was not fully developed because of the attractiveness of the electro-mechanical system described next. The heating and cooling pulse requirements are somewhat difficult for a mechanical system, and miniaturization of the nutating disc system would probably be required for satisfactory performance.

- (3) The third pulsing system proposed used electrically operated solenoid valves similar to those used in automobile fuel injection systems. Because of the large size and temperature limitations of most state of the art valves, it was of doubtful feasibility without development. However, a valve supplied by ANGAR Scientific Corporation shown in Figure 9 appeared to meet the requirements. It had the specified capability of opening and closing in 4-milliseconds. The only unknown quantity was its operating temperature capability. It was cycled in an oven at approximately 160°C for over 48 hours. At the end of this time, it had not failed electrically, but the solenoid was stuck closed. At lowered

temperatures it freed itself and continued to operate satisfactorily. This problem has been remedied by use of a high temperature lubricant. Most of the subsequent testing has been at a temperature level of less than 110°C , although some cycle testing has resulted in valve temperatures above 130°C .

Solenoid valves for steam heating are used to directly spray a mist of dry steam onto the ferroelectric target. However, the saturated water for cooling requires a method of atomizing the water to a fine spray to impinge on the target. Small paint-spray types of nozzles were tried but they require fairly large volume output to achieve a proper spray pattern. To avoid this, the air brush technique is being used in combination with the solenoid valves. A pulse of hot water is injected in the air stream on the target for a cooling spray.

- (4) The system presently being utilized for thermal cycle testing of ferroelectric materials is shown in Figures 9 and 10. The center target area is interchangeable for mounting any combination of dimensions of different ferroelectric materials up to about 3 inches. There are two chambers separated by a seal to keep one side moisture free so that temperature measurements can be made with the IR detector from one side. The heating and cooling vapors are sprayed from one side only. When temperatures are measured by thermocouples (at low cycles of 10 Hz or less)

REVISIONS			
ZONE	LTR	DESCRIPTION	DATE
1	A		8-17-78

CITY ALBANY	CODE 62-11	PART OR IDENTIFYING NO.	NOMENCLATURE OR DESCRIPTION
UNLESS OTHERWISE SPECIFIED DIMENSIONS ARE IN INCHES TOLERANCES ARE: FRACTIONS DECIMALS ANGLES		PARTS LIST	
MATERIAL N/A		CONTRACT NO.	POWER CONVERSION TECH. INC.
FINISH N/A		APPROVALS DATE 9-7-78	INSTALLATION DWG. SOLID STATE HEAT ENGINE THERMAL CYCLE TEST
NEXT ASSY USED ON		SIZE D	CODE IDENT NO. 00043
APPLICATION DO NOT SCALE DRAWING		SCALE N75-	SHEET 1 OF 1

FIGURE 10A

heating and cooling from opposite sides is possible.

It was found that water attacked junctions between thermocouple wires and the sample electrodes. Absorbed water also degrades dielectric properties.

It was recognized that steam and hot water heating and cooling sources will not be satisfactory for future heat engine work. Consideration was given to other chemical combinations which have higher boiling points. However, most of them are of the solvent family and can be toxic and hazardous. However, one family of non-solvent fluids exists that was developed for the electronic industry for atmospheric testing of electronic components at a variety of temperatures. They are known as Fluorinert electronic cooling liquids, manufactured by the 3M Company. They are mixtures of Fluorine compounds and are inert, non-toxic, and odorless. The mixtures result in a range of boiling temperatures and other properties. These properties are shown compared to water in Table 1. It is planned to use the compounds FC-40, FC-43, and FC-70 for heating and cooling of PZT materials which have Curie temperatures in the range of 150°C to 190°C. The fluids can be used directly in the pressure cookers in place of water. The loss of fluid must be carefully controlled since the cost is quite high, being in the range of \$100 to \$300 per gallon. However, the vapor has a much higher density than water vapor and should be easier to condense and collect for return to the system.

TABLE 1
TYPICAL PROPERTIES OF THE "FLUORINERT" LIQUIDS**
AT 25°C,

PROPERTY	FC-88	FC-78	FC-72	FC-77	FC-104	FC-75	FC-40	FC-43	FC-48	FC-70	WATER*
TYPICAL BOILING POINT, °C	30	50	56	97	101	102	155	174	174	215	100
POUR POINT, °C	-115	-73	-90	-110	-65	-88	-57	-50	-62	-25	0 [□]
AVERAGE MOLECULAR WEIGHT	290	300	340	415	435	420	650	670	525	820	18
SURFACE TENSION dynes/cm	9.5	13	12	15	14	15	16	16	19	18	72
CRITICAL TEMPERATURE, °C	150	181	178	251*	230*	227	277	303*	320*	337*	374
CRITICAL PRESSURE, ATMOSPHERES	21.0	19.4*	18.1	14.8*	15.5*	15.8	14.6*	14.1*	13.6*	6.7*	218
REFRACTIVE INDEX (N _D)	1.238	1.267	1.251	1.280	1.271	1.276	1.290	1.291	1.312*	1.303	1.333
ACOUSTIC VELOCITY meters/sec	474	553	512	595	575	585	640	655	707	687	1498
VAPOR PRESSURE, torr	610	274	232	42	29	31	3	1	3	<0.1	23
SOLUBILITY OF WATER ppm	7	14	10	13	11	11	7	7	9	8	Complete
SOLUBILITY OF AIR ml./100 ml.	54	54	48	50	38	40	27	26	35	22	1.9
DENSITY, g/ml.	1.63	1.70	1.68	1.78	1.76	1.76	1.85	1.86	1.94	1.94	1.0
VISCOSITY, centistokes	0.4	0.4	0.4	0.8	0.8	0.8	2.4	2.6	3.1	13.4	0.9
SPECIFIC HEAT, cal./lg) (°C)	0.26	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.24	0.25	1.0
HEAT OF VAPORIZATION AT B.P. cal/g	21	25	21	20	22	21	17	17	19	16	540
THERMAL CONDUCTIVITY milliwatts/(cm ²) (°C/cm)	0.55	0.62	0.57*	0.64	0.64*	0.64	0.66*	0.67	0.72*	0.71*	5.86
COEFFICIENT OF EXPANSION ml./ml.) (°C)	0.0016	0.0016	0.0016	0.0014	0.0014	0.0014	0.0012	0.0012	0.0011	0.0010	0.0002
VOLUME RESISTIVITY ohm-cm.	5.6x10 ¹⁵	9.0x10 ¹⁵	1.0x10 ¹⁵	1.9x10 ¹⁵	8.4x10 ¹⁵	8.0x10 ¹⁵	4.0x10 ¹⁵	3.4x10 ¹⁵	4.2x10 ¹⁵	2.3x10 ¹⁵	not available
DIELECTRIC STRENGTH 0.1in. GAP, KV (RMS)	48	40	38	40	41	40	46	42	47	40	not available
DIELECTRIC CONSTANT (1 KHz)	1.72	1.81	1.76	1.86	1.86	1.86	1.89	1.90	1.94	1.98	78
DISSIPATION FACTOR 1 (KHz), Tan δ	<.0003	<.0003	<.0003	<.0003	<.0001	<.0001	<.0003	<.0001	<.0003	<.0001	not available

* Estimated Values

** Not for specifications purposes. See specification section.

□ Freezing Point

■ Distilled Water

(from 3M CO. literature)

The system shown in Figure 9 has been constructed and operated and is continuously being modified for improved cycle testing. The difficulties experienced with an experimental demonstration system are usually associated with simulation of the final system design and measurement of cycle phenomena. These difficulties usually do not exist in the operation of the final heat engine concept, fortunately. However, they do result in delays in experimental demonstration. The experience with this experimental system will be fully utilized for further development of the staged heat engine experimental demonstration.

3.3 Control and Driving Circuitry

Control of the heating and cooling pulses are indicated by the "valve timing" section of the instrumentation block diagram, Figure 11. The heart of the system is the internal clock. The valve solenoids are driven by pulses independently delayed and adjusted in duration. It will be realized that the output power of the tiny sample under study will be swamped by losses in the system. Therefore, the charging and discharging of the sample must be driven. This is accomplished by a specially constructed Sawyer-Tower like circuit which permits the insertion of a hysteresis controlling inductor in series with the sample. The circuit is operated at an arbitrary frequency synchronized with the internal clock. Sine, triangular, and square wave forms can be used.

VALVE TIMING
INSTRUMENTATION

FIGURE 11

CONTROL BLOCK DIAGRAM

3.4 Diagnostics

General

The proposal (PCT-2-77) presented a derivation of an entropy density equation (3.6 on proposal page 23) based upon reversible processes within a ferroelectric material. The irreversible processes were excluded as small because it was expected that we would operate near the Curie temperature and that 90% of the remaining hysteresis losses could be removed by external circuit inductive control. Deterioration of pressure seals on the heating and cooling fluid handling equipment had, at the time of the measurements, prevented us in most cases from operating higher than about 40°C below the Curie temperature. Furthermore, circuit changes have so far been able to remove only a few percent of hysteresis loss. (Details of this are discussed in Appendix A where it is shown that nonuniformity of sample doping would account for this problem.) Thus, irreversible processes are very much with us. Under these circumstances one may ask, "Is proposal equation 3.6 and its integral form valid?" The basis of the derivation was, in fact, the Gibbs equation (Eq.3.2 on proposal page 22) which remains valid even in the presence of irreversible processes (provided that changes are not too violent) though it applies only to each region of the sample separately¹:

$$S_i = \frac{\gamma \sigma_i^2}{2} + C_o \ln (T/T_{\text{reference}})$$

where the temperature of the various regions are equal. The

entropy of the whole sample is the sum of the entropies of the separate regions:

$$AS = \frac{\gamma}{2} \sum_{i=1}^N A_i \sigma_i^2 = AC_o \ln (T/T_{\text{reference}}) \quad (4)$$

where the area of the total sample is $A = \sum A_i$. The trouble, of course, is that it is not possible for us to measure each of the σ_i^2 's separately; the sample is small enough as it is without cutting up the electrode area into small regions whose outlines we don't even know. What it comes down to is that we measure $A\sigma = \sum \sigma_i A_i$ and estimate $\sum A_i \sigma_i^2$ by $A\sigma^2$. How close is the square of the sum to the sum of the squares? To answer that, we need to estimate the statistical spread of the σ_i 's.

The different regions, i , are characterized by the various doping levels that are found within the sample. For the kind of material utilized in the thermal cycle, separate measurements indicated a standard deviation of 16°C in Weiss temperatures. Since a 1% change in a site doping level of the basic lead titanate material produces about a 10° change in Curie temperature, we may infer that the sample had about a 1.6% spread in doping. This is so small a variation that little difference between the σ_i 's would occur except in the region of instability, that is at the field strength for which $\frac{\partial V'}{\partial \sigma_i} = 0$. These critical values of field strength differ slightly for the different regions so it would be possible at some field for half the polarizations to be reversed.

In such a case, σ^2 would be near zero but $\sum \sigma_i^2$ would be quite different from zero. How can we prevent this? When one of the regions starts to reverse its polarity, it draws current either from the external circuit or from adjacent elements. If the adjacent elements supply the current, then the external circuit loses its control of the instability. This control can be regained if the sample is driven so hard that the applied voltage goes over the instability threshold for most of the elements before any one of them has time to reverse its polarity. This was done by the driving circuitry described in the previous section (3.2). Evidence that it occurred is provided by the oscillogram of Figure 12 which shows the reversal of voltage change right after a knee of the hysteresis curve. The near zero voltage (which held for a relatively long time as indicated by the trace brightness) is evidence that some of the regions reversed their charge together. Still, the hysteresis loop is not symmetrical, indicating that some regions did not reverse polarity at all. The asymmetry could have produced excessively large indicated entropy changes. This was prevented by subtracting its average value out of the varying charge before squaring.

The "S" cycle block of the instrumentation diagram, Figure 13, shows "A" and "B" inputs. The "A" input receives a voltage proportional to temperature from the IR detector. The "B" input receives a voltage proportional to current leaving the sample. After gain to match required operating limits, the "A" signal is put into a linear amplifier representing the appropriate section of a logarithmic response. The "B"

FIGURE 12

Hysteresis loop for material used for the tests
in Figure 17-19.

Vertical axis: 0.05 C/m^2 per division

Horizontal axis: 484 kv/m per division

signal is integrated to give a voltage proportional to $-\sigma A + \bar{\sigma} A$ and then squared. These two signals are added in amplifier C. The output of C is sampled repeatedly at a given phase in the thermal cycle operation. This phase is then gradually shifted in synchronism with a similar sampling process which occurs with the vertical input to the oscilloscope driven by the temperature signal in channel A. All of the electronics are direct coupled to eliminate any undesired reactances which could incorrectly produce open loop areas in the display.

Calibration

First, simulated voltages were used to check the linear, quadratic, and integrating circuits both for magnitude and proper phase of response. An example is provided by Figure 14 which shows an early oscillogram of the response function of the logarithmic amplifier taken with a 16 Hz sinewave input. Quite obviously it generates its own open loop. To permit such operation would invite erroneous interpretation of our thermal cycle results. The condition was corrected by removing noise integrating capacitors from the A input section and using the linear approximation $\ln(1 + \frac{\Delta T}{T}) = \frac{\Delta T}{T}$ to avoid the "touchy" log amplifier. To minimize random noise we used a sampling system to remove noise on the output.

Calibration of the "A" input gain was performed by correlating the roughly calibrated IR detector output with a known 0.002 inch diameter thermocouple. (A small diameter

INCORRECT EARLY CURVE SHOWING PHASE LOOP WHICH HAD TO BE
ELIMINATED

FIGURE 14

thermocouple is necessary to respond to the rapid temperature changes.) This thermocouple response was 3 milliseconds; 10% to 90% of the voltage waveform. The IR detector with a 1×10^{11} amplification factor also had a 3 millisecond, 10% to 90% response.

Dry steam at 101°C was applied to the back side of a blackened 0.01 inch thick copper window with the IR detector on the other side. The background temperature was 91°C. The thermocouple indicated a 5°C change and the IR detector indicated a 79 millivolt change, therefore,

$$\frac{.079}{5^{\circ}\text{C}} = 15.8 \text{ mV}/^{\circ}\text{C}.$$

The "B" input was calibrated to read charge at the output of B, (Figure 13) versus the input voltage across a one kilo-ohm resistor in the Sawyer-Tower circuit (see also Figure 11 "Overall Instrumentation Block Diagram", and Calibration Curve Number 2, Figure 15).

To make the entropy plot on the oscilloscope the "S" cycle electronics, external sample-hold and driver, Sissors amplifier, one-shot trigger drive and IR detector must be time correlated with the valves. One function of the clock is to trigger the fast ramp generator. The fast ramp time of duration is picked so that more than one cycle is enveloped by its duration (reference Figure 16). The output of the Sissors amplifier is a result of subtraction of the fast from the slow ramp; the output of this high gain

FIGURE NO 16
TIME COORELATION

amplifier switches from its positive saturated value to its negative saturated value when the two ramp voltages are equal. This triggers a 200-milliamp one-shot which keeps the oscilloscope and the sample-hold amplifiers in proper sampling time phase. Figures B2 and B3 have been included to give greater detail on the instrumentation package.

3.5 Measurements

As discussed earlier, we have a rough measure of entropy but we do not have independent control of entropy because of the hysteresis dissipation within the sample. It has thus been difficult to obtain the square shaped T-S loops aimed at in this work. Yet, we have obtained in one case a power production efficiency nine times the Van der Ziel limit. We expect to obtain a roughly square loop T-S diagram when we get some very pure, high polarization material. Then the stage efficiency would rise to ten times the Van der Ziel limit and with the lead titanate material being prepared for us by the Ames Research Center we expect to approach 100 times the Van der Ziel limit.

Figures 17 through 19 show a sequence of energy cycle measurements taken with three different values of the heating pulse delay relative to the peak charge on the sample. (The cooling for these cases was provided by a steady air flow). The left member of each pair of photos is the scope sampled and averaged raw data. Two electrical and four thermal cycles are shown. They represent averaged sampled value from approximately 1200 electrical and 2400 thermal cycles. The rough curves are IR detector outputs proportional to the negative of temperature excursions. The smooth curves are proportional to $(\sigma - \bar{\sigma})^2$. The right member of each pair of photos is a computer reduction of data from the first

FIGURE 17A

FIGURE 18A

FIGURE 19A

FIGURE 17-19

. Sampling scope oscillogram of I.R. detector output (proportional to negative of temperature change) and charge change squared ($0.035 \text{ C}^2/\text{m}^4$ per division) versus time during a thermal cycle.

FIGURE 17B

FIGURE 18B

FIGURE 19B

FIGURE 17-19

B. Resulting temperature versus entropy plots.

cycle shown by the left photo. The proper temperature component of the entropy has been added in and the temperature plotted versus entropy. Unfortunately, the top two curves were executed in a counter-clockwise direction so the efficiency is shown as negative. The third curve is a figure-eight; the top loop was executed clockwise and the lower one counter-clockwise.

We were able to exert more control over the thermal cycle when we pulsed a cooling spray onto the sample. Then the thermal cycle was executed in a clockwise direction. An example is shown in Figure 20. The loop is slanted, due in part to the hysteresis production of entropy. Yet, we were able to obtain much greater efficiency than the use of sinusoidal heating with continuous radiant cooling proposed by Van der Ziel. The most spectacular departure from the "ideal" Van der Ziel cycle is the enormously greater power production density which was obtained with this cycle, 167 kW/m^3 versus about 1 kW/m^3 for the Van der Ziel cycle. In addition to the efficiency factor, the difference is due to use of the whole polarization change possible with the material and to cycling our capacitor many times faster than the "optimum" frequency computed for Van der Ziel's cycle. The hysteresis loop for the material used for this test is shown in Figure 21. We often found that under the action of heating and cooling pulses, the charge change was roughly doubled over that measured in passive hysteresis loops approaching the 0.31 C/m^2 found in the remnant polarization measurements.

FIGURE 20
TEMPERATURE VERSUS ENTROPY CYCLE

FIGURE 21
HYSTERESIS LOOP FOR PZT MATERIAL
USED IN FIGURE 20
Vertical axis: 0.1 C/m^2 per division
Horizontal axis: 939 kv/m per division

IV PERFORMANCE, PROJECTIONS, AND PROBLEMS

4.1 Comparison of Measured Performance with Predictions

Engine cycle efficiency is given by Eq.(2.8) on page 17 of the proposal. Using the parameters of the material with which the cycle test was conducted, $\gamma = 2.9 \cdot 10^5$ meters/farad kelvin, $C_O = 2.8 \cdot 10^6$ joules/m³ kelvin and $\sigma_{\max} = 0.31$ coulombs/m² the calculated efficiency is 0.26%. The difference is partly caused by the less-than-optimum shape of the cycle. We are currently revising our design of the delay networks from analog to digital to correct this.

The horizontal scale of the cycle diagrams are about what would be expected from theory for this material, $-\frac{\gamma}{4} \sigma_M^2$, though this may have been fortuitous.

Hysteresis losses were only reduced by a few percent against the projected 90% control. This can, we believe, be greatly improved by use of materials having doping uniformity to about 50 parts per million.

4.2 Projections

We see clear changes which can be expected to improve the heat transfer timing. Indications from the extent of the measured cycle are that nearly full theoretical efficiency and power production density can be achieved by this means. The frequency of the thermal cycles is presently limited to about 25 Hz for solenoid valve operation. Use of reeds replacing the present valves should allow operation to the desired 120 Hz. The 10 mil PZT material had ample strength but we anticipate mechanical strength problems which would place a practical lower limit of about 5 mils on dielectric thickness. This might require a reduction in frequency to about 60 Hz thermal (30 Hz electrical) for nearly full efficiency operation.

On the assumption that the required degree of doping homogeneity will not be economically practical, we will have to operate above the Curie temperature at a loss of about 25% in efficiency and 50% in power density. On the other hand, new materials are coming to fore¹ which have remnant polarization densities about four times as much as that of the lead titanate used for examples worked out in the proposal. Were they available, these materials would improve efficiency per stage to about 9 1/2% (up to working temperatures of about 200°C) and power density to about 15 times as much as the figures given in the proposal. Combining these prospects with the above mentioned reductions leads to projected performance of about 7% per stage and a power handling capacity of about 7 times as great as previously projected. However we feel uncomfortable with such a forecast depending, as it does, on a single unconfirmed report.* we therefore return to our previous forecasts with the feeling that both positive and negative changes are likely in the practical material parameters that will be available within the time span of this contract. It seems to us that a $\pm 30^\circ$ margin of error would be reasonable in the projection for a power converter which could be made starting with materials that experience will have been obtained by the end of the contract period.

* It should be noted however, that this article was published in an established archival journal by three authors two of whom have published at least four related articles in this and other journals.

4.3 Problems

Ferroelectric Materials

The ceramic ferroelectric materials that were evaluated were obtained from several manufacturing sources which included the following:

1. EMCON division of Illinois Tool Works (BaTiO_3 compounds)
2. CENTRALAB Division of Globe Union (BaTiO_3 compounds)
3. GULTON INDUSTRIES.- Piezoelectric Division (PZT compounds)
4. VERNITRON Piezoelectric Division (PZT compounds)

The materials from the above manufacturers were obtained from their on-hand stock and do not necessarily meet specifications required for a ferroelectric heat-to-electric conversion system. In addition, materials were received from EDO Corporation, Motorola, Sandia, and Vernitron through the University of Illinois. These materials were first evaluated by the University of Illinois for ferroelectric properties. Some of the materials were coated with various thicknesses of silver, nickel, or aluminum electrodes. The thicknesses of the ceramic materials varied from about two mils ($\sim 50 \mu\text{m}$) to greater than 20 mils ($> 500 \mu\text{m}$).

One of the methods employed to fabricate these piezo-ceramic materials is to lay down many thin layers of less than 1 mil ($< 25 \mu\text{m}$) in the green state on top of each other and then furnace sinter in several stages. Thus it would seem a simple matter to produce thin discs and plates of ferroelectric. However,

thin layers are less resistant to the residual stresses that build up during sintering, resulting in a curling up of the edges. The problem becomes more severe for larger sheets (greater than four inches) resulting in shattering upon cooling down. The deformation problem is thought to be due to both residual thermal stress and stress due to porosity formation and non-uniform shrinkage. However, it is generally thought that fabrication techniques can be developed for production of large thin sheets that are flat. Some of the techniques that indicate promise are:

1. Staged sintering and cooling to reduce thermal stress buildup.
2. Isostatic hot pressing to achieve high density (low porosity) and smaller, more uniform pore size. Current commercial materials typically have pore sizes of 1 to 2 μm with 95 to 97% theoretical density. The results of vacuum processing development is reported in reference 2 and 3 on PLZT ceramic. By hot pressing in a vacuum of 10^{-4} Torr for approximately 1 hour followed by air sintering for times up to 40 hours, they obtained pore-free structures.
3. Vacuum sintering of the green ceramic to achieve nearly pore-free ceramic ferroelectric structure. Again in reference 2 by sintering in medium vacuums of only 1 to 10 Torr, the porosity was reduced by more than one order of magnitude. The density was greater than 99.8% of theoretical.
4. Other vacuum deposition techniques that may have promise are sputtering in vacuum or partial vacuum. Much thinner layers can be deposited resulting in more uniform and repeatable ferroelectric properties and predictably greater strength. Some preliminary work is reported in the reference 5.

It is expected that development of the above manufacturing techniques will result in higher strength ceramic ferroelectrics that are less fragile (see Figure 22 for an array of typical samples after moderate handling by PCT). It is not known exactly what tensile strength the materials must possess, but it should exceed $8 \times 10^6 \text{ n/m}^2$ (15,000 psi). Some experimental measurement of ceramic ferroelectric strength has been done in references 4 and 5. The work in these references shows the following effects on strength.

1. Internal stresses between grains and material flaws from manufacturing seriously degrade the ceramic ferroelectric tensile strength.
2. The mechanical strength of BaTiO_3 tested at room temperature exceeds $8 \times 10^6 \text{ n/m}^2$ (15,000 psi). However, it is concluded that the internal stresses between grains exceeds $32 \times 10^6 \text{ n/cm}^2$ (60,000 psi).

Some bench tests were conducted on ceramic ferroelectric materials using the three loading techniques shown in Figures 23, 24, and 25. Dead weight static loading with sand and lead shot were used with the Figure 23 tests. The structural equations to predict failure were those of reference 1 and 8. The ceramic materials were Barium Titanate (BaTiO_3) and Lead Zirconium Titanate (PZT). The stress predicted by the equations at failure was around $4 \times 10^6 \text{ n/cm}^2$ (7,500 psi) for BaTiO_3 and 8×10^6 (15,000 psi) for PZT. It is noted in reference 7 that the equations are valid up to the yield (elastic) stress only for thin ductile materials which deflect excessively before failure. It is noted also in reference 7 that the elastic

FIGURE 22
TYPICAL TEST SPECIMENS

$$a = b = 13/16 \text{ inch}$$

$$S_{\max} = \frac{1.2778 p a^2}{t^2}$$

p = Load per Unit Area

$S_{\max}$ = MAXIMUM TENSILE STRENGTH

FIGURE 23
FLAT PLATE BENDING STRENGTH TEST SCHEMATIC

FIGURE 24
BEAM BENDING STRENGTH TEST SCHEMATIC

$$S_{\max} = \frac{3 p d^2}{16 t^2} \text{ (tensile strength)}$$

$d = \text{Disc Diameter}$

$t = \text{Disc Thickness}$

FIGURE 25
BURST TEST FIXTURE FOR STRENGTH TESTING

equations can be used to predict failure at the ultimate strength of brittle materials which have no yield points⁷. Most of the existing ceramic piezoelectric materials are in this category. The bench tests were conducted on Barium and Lead-Zirconium Titanate. To verify these tests, the tests of Figure 25 were repeated for thin metal foils of aluminum, copper, and tungsten which have well-known room temperature ultimate tensile strengths. The load resisted by the aluminum (25 μm) and copper (38 μm) was at least an order of magnitude above that predicted by the equation. Even the tungsten sheet of 25 μm (normally considered brittle) deflected noticeably and resisted loads 3 to 4 times that predicted.

It is believed that the direction of materials development for improved ferroelectric structural performance should be toward less fragility or more ductility (as relative to extreme brittleness). This is analogous to the materials development of cast iron and the formerly brittle refractory metals (such as molybdenum and tungsten) and ceramic insulators (Aluminum Oxide and Beryllium Oxide). Relatively ductile forms of these materials which retain their other advantageous properties have been developed by using vacuum processing techniques. Again, the preliminary work done in references 2, 3 and 5 shows improvement in piezoelectric ferroelectric properties by vacuum processing. It might be possible to obtain ultimate tensile strengths in the bending mode that would exceed 80,000 psi ($32 \times 10^6 \text{ n/cm}^2$) if the residual grain boundary stresses

could be eliminated during manufacture. Although it is possible that the resulting material might not be a good piezoelectric material, perhaps it would retain its ferroelectric properties. Perhaps the voltage breakdown strength could also be increased with the development of processing techniques.

Thermal Control

As predicted by one of the referees, we are experiencing difficulty in precisely controlling the delivery and extraction of heat at specific times and temperatures. This now looms as a major problem facing us in Phase IB.

V . SUMMARY & CONCLUSIONS

The Van der Ziel limiting efficiency for pyroelectric material has been exceeded by a factor of nine due to a thermal cycle improved over the one proposed by Van der Ziel. The efficiency reached 88% of that projected for a material having parameters of those tested. The density of power conversion has exceeded by more than a factor of 10 the limit implied by the Van der Ziel formulas due to our use of the full polarization change of the ferroelectric material rather than the linear change studied by Van der Ziel, as well as use of the higher efficiency and higher frequency. The power conversion density is close to that predicted in the proposal. The impedance of the power converter was about 40,000 Ω , very much less than is implied by the Van der Ziel analysis and very much greater than forecast for a working converter in the proposal. This latter occurred because we used for our tests very small but thick samples 5cm² x 10 mils rather than the large arrays of thin samples projected for an operating unit.

In conclusion, the primary demonstration goals for Phase 1A have been met with little need to modify projections of ultimate usability. However, we have met a serious requirement for much greater material purity than is commonly encountered in samples which have been available to us.

APPENDIX A

INDUCTIVE CONTROL OF HYSTERESIS

A.1 Origin of Hysteresis

Minimizing the free energy of a ferroelectric crystal leads^{A1} to the following static relationship between field strength, E_p , and polarization density, p :

$$E_p = (T - T_0) \gamma p - B p^3 + C p^5 \quad (A.1)$$

where γ , B , and C are often referred to as Devonshire's coefficients and T_0 as the Weiss temperature. This equation is shown graphically in Figure A.1. This form of the relationship has been well confirmed experimentally^{A2} for regions where $\frac{dE}{dp} > 0$. The other regions, where $\frac{dE}{dp} < 0$, are unstable in a simple circuit in which the field strength is supplied by a low impedance source. Equation (A.1.) does not take into account dynamic effects such as frictional processes during polarization change. Friction is sometimes so small that polarization can completely reverse in a few microseconds^{A3}. If the external circuit is such as to permit this maximum rate of reversal, the small friction factor giving rise to a field E_v will be responsible for a very significant energy dissipation within the crystal:

$$W = \int_{-p_M}^{p^*} E_v dp \quad (A.2)$$

where p_M is the value of p for which $\frac{dE}{dp} = 0$, and p^* is the stable value of p at the same field.

In a typical test circuit (Sawyer-Tower or battery driven), the total applied field, $E = E_p + E_v$, at which the (A.3)

FIGURE A1 PLOT OF POLARIZATION DENSITY VERSUS STATIC FIELD STRENGTH ACCORDING TO EQ A.1 with $T-T_0 = -5^\circ$, $\gamma = 4 \times 10^5$, $B = 6 \times 10^8$, and $C = 9 \times 10^9$ (S.I. units). The dashed vertical lines indicate the paths of abrupt transition which occur in conventional circuits.

switching begins, does not change significantly during the switching time. Thus, energy loss in a complete cycle

$$(-p_M, +E_M), (+p^*, +E_M), (+p_M, -E_M), (-p^*, -E_M), (-p_M, +E_M)$$

is given by: $w = \oint (E - E_p) dp = \oint E dp$ (A.4)

This is the area of the hysteresis loop as determined by the knees of the curve represented by Eq. (A.1) without regard to the particular form of the dependence of the frictional field, E_v , on $\dot{p}$ provided that switching is fast compared with changes in the applied field, (see Figure A1). We may also note that the only property of $E_p(p)$ actually required for its cyclic integral to equal zero is single valuedness of E_p versus p . Even though Eq.(A.1) predicts regions of negative slope, it is clear that observations in ordinary circuits will not reveal this, but rather will yield the familiar hysteresis loop.

It is the purpose of the present Appendix to discuss the use of non-standard external circuits to obtain control of the hysteresis process. Before proceeding with that however, we should note a departure from ideal behavior which can be observed for many ferroelectric samples directly with the standard circuitry. While some samples are reported to have very fast spontaneous switching times, the samples that we have had to work with in the laboratory have, for practical purposes, infinite spontaneous switching times. That is, the sides of the hysteresis loops are not vertical, but have positive slope; switching must be driven (see Figure A2). How can we account for this? The samples we have obtained

440 micro-
seconds per dot

FIGURE A2 a

FIGURE A2 b

BLOCK DIAGRAM OF CIRCUIT USED TO DISPLAY SWITCHING
TIME OF A SAMPLE OF PZT MATERIAL. ILLUSTRATED IN
WAVEFORM ABOVE.

PZTG 1195
 $\tau = 116 \mu\text{sec}$
 $\tau_s = .768 \text{ ms}$

FIGURE 2C

FIGURE A2 c

PZTG 1278
 $\tau = 116 \mu\text{sec}$
 $\tau_s = .676 \text{ ms}$

FIGURE 2D

FIGURE A2 d

$$\tau_s = \frac{Q_{\max}}{I_{\max}}$$

PSZTU

$$\tau = 116 \mu\text{sec}$$

$$\tau_s = 1.011 \text{ ms}$$

FIGURE A2 c

BaTiO₃

$$\tau = 239 \mu\text{sec}$$

$$\tau_s = 2.748 \text{ ms}$$

FIGURE A2 f

PSZTU

$$\tau = 184 \mu\text{sec}$$

$$\tau_s = .950 \text{ ms}$$

FIGURE A2 g

$$\tau_s = \frac{Q_{\max}}{I_{\max}}$$

are apparently from batches having values of Curie temperatures scattered about their nominal value. In one case, we got enough samples to make a statistical analysis which is summarized in Figure 2. Like most of our material samples, they were supplied by a commercial firm (in many cases via the University of Illinois). These firms have interest in minimizing the temperature dependence of the capacitors they manufacture. Thus, heterogeneous doping of the ferroelectric to produce a spread of T_0 and hence of Curie temperatures would be desirable from their point of view. However, our needs are for highly temperature dependent capacitors for use in the heat engine. If the spread of curie temperatures we have found between samples is representative of the spread of T_0 within single samples, it would be difficult for us to make efficient use of these materials. In order to evaluate the performance expected from such samples, we have made the following model of a capacitor composed of heterogeneously doped ferroelectric. Each sample capacitor consists of ten small, parallel capacitors having a statistical distribution of Weiss temperatures. For each element, we will have:

$$E_i = (T - T_i) \gamma p_i - B p_i^3 + C p_i^5 \quad (A.5)$$

The charge on the sample is given by:

$$q = \sum_{j=1}^N \sigma_j A_j \quad (A.6)$$

where σ_j is the surface charge density on the j 'th capacitor having element area A_j . The total area is:

$$A = \sum_{j=1}^N A_j \quad (A.7)$$

and the average surface charge density is:

$$\sigma = q/A \quad (\text{A.8})$$

Poisson's equation for polarizable matter is:

$$\epsilon_0 \vec{\nabla} \cdot \vec{E} = \rho - \vec{\nabla} \cdot \vec{p} \quad (\text{A.9})$$

where ρ is volume charge density. It is sometimes true that $\rho \neq 0$ in the volume of dielectrics, but we will assume for simplicity that $\rho = 0$ within the dielectric volume and that integrating ρ from $y = 0^-$ (in the dielectric just below the surface) to $y = 0^+$ (in the electrode just above the surface) gives an effective surface charge density:

$$\int_{\substack{\text{outside } i \\ \text{inside} \\ \text{element } i}} \rho \, dy = \sigma_i \quad (\text{A.10})$$

We will also take the situation where $E = 0$ in the electrode outside the sample and is uniform within it:

$$0 - E_i = \int_{\substack{\text{outside } i \\ \text{inside} \\ \text{sample } i}} \vec{\nabla} \cdot \vec{E} \, dy = +V'_i \quad (\text{A.11})$$

where V'_i is the voltage gradient within the sample element. Thus, upon integration, Equation (A.9) yields:

$$p_i = -\sigma_i + \epsilon_0 V'_i \quad (\text{A.12})$$

The largest field strength to be employed in practice is of the order of about fifteen megavolts per meter corresponding to a polarization density, $\epsilon_0 V'_i$, of about 10^{-4} coulombs per square meter which is much smaller than the range of polarization densities which occur in ferroelectrics. Thus the second term on the right side

of (A.12) can be neglected and Equation (A.5) becomes

$$V'_i = (T - T_i) \gamma \sigma_i - B \sigma_i^3 + C \sigma_i^5 \quad (\text{A.13})$$

In a static situation with the sample electroded so that all the V'_i 's are equal, Equation (A.13) must be solved for σ_i and Equations (A.6) through (A.8) used to plot V' versus σ . This is done in Figure (A.3). Compare this with Figure (A.1). From this we can extrapolate to a continuous distribution of Weiss temperatures which could be expected to yield the kind of sloping sided hysteresis loops we observed.

The observed slopes like that shown in Figure A2. can be quantitatively related to the statistical distribution of Weiss temperatures and hence to Curie temperatures. Measurements of Curie temperatures versus doping levels could then be used to infer the statistical distribution of dopant.

The change in average charge which occurs when a small group of elements switch polarity is:

$$d\sigma = \Delta\sigma(V') f[T_i(V')] dT_i = \Delta\sigma(V') f[T_i(V')] \frac{dT_i}{dV'} dV' \quad (\text{A.14})$$

where $\Delta\sigma(V')$ is the magnitude of the change in σ for those elements having $\frac{dV'}{d\sigma_i} = 0$ at the particular value of gradient, V' ,

and $f(T)$ is the normalized distribution of Weiss temperatures,

$$\int_0^{\infty} f(T_i) dT_i = 1 \quad (\text{A.15})$$

From Eq(A.13) we obtain

$$\frac{dT_i}{dV'} = \frac{-1}{\gamma \sigma_i} \quad (\text{A.16})$$

where σ_i is evaluated where $\frac{dV'}{d\sigma_i} = 0$.

FIGURE A.3 AVERAGE SURFACE CHARGE DENSITY VERSUS STATIC VOLTAGE GRADIENT IN A MATERIAL CHARACTERIZED BY THE SAME DEVONSHIRE COEFFICIENTS AS THOSE USED IN FIGURE 1 BUT WITH A DISTRIBUTION OF TEN WEISS TEMPERATURES. EACH VALUE OF T_0 WAS LOCATED AT THE MEDIAN POINT OF 1.0% OF THE AREA OF A NORMAL DISTRIBUTION. THE DISTRIBUTION WAS CENTERED AT THE OPERATING TEMPERATURE AND HAD A STANDARD DEVIATION OF 5°C .

Combining Eqs.(A.14) and (A.16),

$$f(T_i) = - \frac{\gamma \sigma_i}{\Delta \sigma_i} \frac{d\sigma}{dV'} \quad (A.17)$$

The factor $F = - \frac{\gamma \sigma_i}{\Delta \sigma_i}$ is always positive for when σ_i is positive,

$\Delta \sigma_i$ is negative representing the sudden reversal of polarity of the element, i. The 'F' changes little over the range of interest. For material characterized by the Devonshire coefficients used in Figures A.1 and A.3, $F = 1.76 \cdot 10^5 \pm 6\%$ (S.I. units) over the range of $|V'|$ from $2 \cdot 10^5$ to $3 \cdot 10^6$ volts/meter as shown in Figure (A.4). This figure also gives the Curie temperature which corresponds to each field strength along the slope.

A.2 Inductive Control

For dynamic situations, we must include the frictional field, E_v . As discussed before, the exact form of the dependence of E_v on $\dot{p}$ or $\dot{\sigma}$ is probably not very important, so we choose a simple ohmic form:

$$V'_v = \rho \dot{\sigma} \quad \text{where } \rho \text{ here represents an effective resistivity.} \quad (A.18)$$

For each element of the capacitor, we have:

$$V = R_i \dot{\sigma}_i A_i + f_i(\sigma_i) = 1/N \sum_{j=1}^N \{ R_j \dot{\sigma}_j A_j + f_j(\sigma_j) \} \quad (A.19)$$

where:

$$R_i = \rho W / A_i \quad (A.20)$$

$$f_i(\sigma) = \{(T - T_i) \sigma - B \sigma^3 + C \sigma^5\} W \quad (A.21)$$

FIGURE A4: CONVERSION FACTOR AND CURIE TEMPERATURE ELEVATION ABOVE MEASUREMENT TEMPERATURE VERSUS VOLTAGE GRADIENT ON A SLOPING HYSTERESIS LOOP (PSZT). THE DISTRIBUTION OF CURIE TEMPERATURES ($T_c = T_i + \frac{B^2}{4\gamma C}$) WITHIN A SAMPLE IS $f(T_c) = F \cdot \frac{d\sigma}{dV}$, FOR DEVONSHIRE COEFFICIENTS GIVEN IN TEXT.

with W the thickness of the capacitor and V the total voltage across it.

In order to exercise control over the hysteresis energy loss, we place an inductor in series with the capacitor. The voltage is then given by:

$$V = -L\ddot{\sigma}A - R\dot{\sigma}A \quad (\text{A.22})$$

where L and R are respectively the inductance and resistance of the coil. Taking the derivative of Eq.(A.19) gives:

$$R_i \ddot{\sigma}_i A_i + f'_i(\sigma_i) \dot{\sigma}_i = 1/N \sum_{j=1}^N [R_j \ddot{\sigma}_j A_j + f'_j(\sigma_j) \dot{\sigma}_j] \quad (\text{A.23})$$

For homogeneous resistivity, ρ , and equal elemental areas A_i , the resistance R_j will be independent of j and so can be removed from under the summation in Eqs.(A.19) and (A.23). The resulting sum is, $\sum_{j=1}^N \ddot{\sigma}_j A_j = \ddot{\sigma}A$ by virtue of Eqs.(A.6) through (A.8).

The product $\ddot{\sigma}A$ can then be replaced using Eq.(A.22). This gives:

$$R_i \ddot{\sigma}_i A_i + f'_i(\sigma_i) \dot{\sigma}_i = -\frac{R_i}{LN} [R_i \dot{\sigma}_i A_i + f_i(\sigma_i) + R \sum_{j=1}^N \dot{\sigma}_j A_j] + 1/N \sum_{j=1}^N f'_j(\sigma_j) \dot{\sigma}_j \quad (\text{A.24})$$

This differential equation was solved numerically for $N=10$ capacitors as shown in Figure (A5). This shows a sequence of half hysteresis loops for increasingly broad Weiss temperature distributions. These distributions correspond roughly to 5, 50, 500, and 5,000 parts per million fluctuation in lanthanum doping within a given sample of lead-titanate. These results

suggest that inductive control can be realized by keeping nearly all the elements of a capacitor at nearly equal charge density, and that this would occur for doping density variations up to about 50 parts per million of the basic material; beyond that significant qualitative changes occur.

FIGURE A5

Effect of the statistical spread (S=Standard deviation of Weiss Temperatures in °C) on the form of discharge of a ferroelectric through and inductive (L=1 henry), resistive (R=66 Ω) circuit.

FIGURE B1
Diagnostic Circuit Schematic

FIGURE B2
VALVE TIMING INSTRUMENTATION SCHEMATIC

FIGURE B3

IR Calibration

Top: Valve Signal to open 5V/div

Bottom: IR Detector

Horizontal 5 ms/div

FIGURE B4

ELECTROCALORIC

0.1V TOP 1 sec sample
averaging

0.1V BOTTOM 7 ms sample
averaging

.012 sec/div or 83.33cy/div
Horizontal

Waveform Horizontal

31.8 hz of Electrocaloric

Input of 15.9 hz at 500V (0-peak) applied to the sample. The input was a square wave. This measurement is made just prior to the "S" plot to verify that the crystal is indeed functioning.

APPENDIX C

MEASUREMENT OF DEVONSHIRE COEFFICIENTS

In order to compare experimental engine performance with theory, the Devonshire coefficients must be obtained for the particular sample in question. In principle this is very easily done by measuring the charge released from the poled sample at near zero voltage as a function of rising temperature and then making a leastsquares fit to the quadratic form in σ^2 ,

$$T = T_0 + \frac{B}{Y} \sigma^2 - \frac{C}{Y} \sigma^4 \quad (C.1)$$

where σ is the charge density remaining at temperature T . If the sample contains a significant spread in T_0 , σ will not drop abruptly to zero at a particular temperature as would be expected for a first order transition. Instead, it will go asymptotically to zero. Values of the Devonshire coefficients can be obtained minimizing the function L :

$$L = \sum_T \left[\sigma(T) - \frac{Q}{A}(T) \right]^2 \quad (C.2)$$

where $\sigma(T)$ is computed from

$$\sigma(T) = \frac{1}{N} \sum_{i=1}^N f_i(T) \quad (C.3)$$

$$\text{with } f_i = \sqrt{\frac{B}{2C} + \sqrt{\frac{B^2}{4C^2} - \frac{Y}{C} (T - T_i)}} \quad \text{where the inner radical is real} \quad (C.4)$$

$$= 0 \quad \text{otherwise}$$

T_i is the i 'th Weiss temperature in a N component model of

the sample. For a normal distribution,

$$T_i = T_o + \gamma_i S \quad (C.5)$$

where S is the standard deviation of the distribution and γ_i are points standing at the centroids of $1/N$ of the area of a normal distribution of unit standard deviation.

For $N = 10$,

$$\begin{array}{ll} \gamma_1 = -1.753 & \gamma_6 = 0.145 \\ \gamma_2 = -1.105 & \gamma_7 = 0.410 \\ \gamma_3 = -0.705 & \gamma_8 = 0.705 \\ \gamma_4 = -0.410 & \gamma_9 = 1.105 \\ \gamma_5 = -0.145 & \gamma_{10} = 1.753 \end{array} \quad (C.6)$$

A computer program was written to minimize L with respect to S , T_o , B/γ and C/γ for material of the type used in the engine producing the thermal cycle shown in Figure 1.

Sixty-two data points were used. (It takes less than one day running time on a basic level II Radio Shack computer iterating twice after the initial minima are obtained).

The results are:

$$\begin{array}{ll} T_o = 177.6^\circ\text{C} & S = 15.6^\circ\text{C} \\ B/\gamma = 236.4 & C/\gamma = 37530 \end{array} \quad (\text{S.I. units}) \quad (C.7)$$

The value of L , summing over all sixty-two points, was 1.754×10^{-3} giving standard error only $0.0052 \text{ coulombs/m}^2$ (or about 2% of the room temperature remnant polarization value).

The value of γ can be obtained by a least squares fitting of the reciprocal of capacitance at the highest temperature range. It was found to be:

$$\gamma = 2.87 \times 10^7 \quad (\text{S.I. units}) \quad (\text{C.8})$$

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APPENDIX A

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