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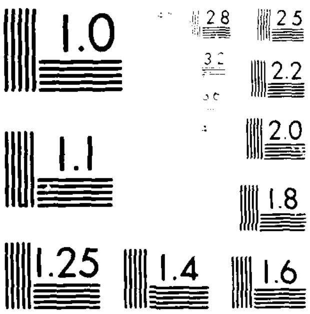

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STUDY OF PYROELECTRIC DEVICES

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Final Technical Report: Part I of 2 Parts

A. van der Ziel

J. H. Judy

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April 1, 1972 - March 31, 1975

Night Vision Laboratory
U. S. Army Electronics Command
Fort Belvior, VA. 22060

Contract No. DAAK02-72-C-0398

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FOREWORD

This investigation was conducted from April 1, 1972 to March 30, 1975 by the Department of Electrical Engineering, University of Minnesota, under Contract DAAK02-72-C-0398 with the Advanced Research Projects Agency. The contracting officers representative is Mr. Edward C. Walker, Night Vision Laboratory, Fort Belvior, Virginia. The final technical report is submitted in two (2) parts.

A. van der Ziel
Principal Investigator
J. H. Judy

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A. Theory of Pyroelectric Detectors

1. The Thermodynamical Approach

In the thermodynamical approach to pyroelectricity one writes the field E in a pyroelectric as an odd function of the polarization P

$$E = \beta(T - T_C)P + BP^3 + CP^5 + \ldots. \tag{1}$$

where T_C is the Curie temperature and β, B and C are constants. We assume that β and B are positive and for the sake of simplicity we first neglect the CP^5 term. For $T < T_C$ the equation $E = 0$ has a non-zero solution for P; in other words, there is a spontaneous polarization P_S for $T < T_C$. $E = 0$ yields

$$\beta(T - T_C)P + BP^3 = 0 \quad ; \quad P = P_S = \left[\frac{\beta(T_C - T)}{B}\right]^{1/2} \tag{2}$$

Hence the pyroelectric coefficient is

$$p = -\frac{\partial P_S}{\partial T} = \frac{1}{2}\left(\frac{\beta}{B}\right)^{1/2} \frac{1}{(T_C - T)^{1/2}} \tag{3}$$

the differential susceptibility is

$$\varepsilon - 1 = \frac{1}{\varepsilon_0 \partial E/\partial P\rceil_{P_S}} = \frac{1/\varepsilon_0}{\beta(T - T_C) + 3BP_S^{\,2}} = \frac{2}{\beta\varepsilon_0(T_C - T)} \tag{4}$$

and the figure of merit of the pyroelectric detector is

$$\frac{p}{\varepsilon^{1/2}} \simeq \frac{p}{(\varepsilon - 1)^{1/2}} = \frac{\varepsilon_0^{\,1/2}\beta}{(2B)^{1/2}} \tag{5}$$

which is independent of the temperature T. Experimentally one finds some decrease in $p/(\varepsilon - 1)^{1/2}$ for decreasing temperature T; most of it comes from the CP^5 term in (1).

This is a thermodynamical theory, and hence it should be correct. Unfortunately the Taylor expansion (1) does not converge too well for large P, and as a consequence (5) (or its equivalent if the CP^5 term is taken into account) is only correct near the Curie temperature. Better agreement away from the Curie temperature might be obtained by using still higher order terms in (1), but this is no guarantee that the Taylor expansion will converge well for larger P.

To carry the theory further it is necessary to express the terms β and B in molecular parameters. Only then can one hope to understand why $p/\varepsilon^{1/2}$ is of the order of 3×10^{-9} Coulomb $\mathrm{cm}^{-2}\,{}^\circ\mathrm{K}^{-1}$. We shall investigate this problem in the next two sections.

2. Molecular theories

We shall now discuss two theories that allow the expression of β and B in terms of molecular parameters. To that end one writes for the potential energy V(x) of an ion in the crystal

$$V(x) = \frac{1}{2} f_0 x^2 + \frac{1}{4} g_0 x^4 + \frac{1}{6} h_0 x^6 + \ldots. \qquad (6)$$

where f_0, g_0 and h_0 are constants and x is the deviation from equilibrium in the X-direction. To simplify matters, we ignore the sixth order term in (6). We then have two possibilities:

1) $f_0 < 0$, $g_0 > 0$. In this case V(x) has a minimum when $dV/dx = 0$, or

$$f_0 x + g_0 x^3 = 0 \quad ; \quad x = x_0 = \pm \left(\frac{-f_0}{g_0}\right)^{1/2} \qquad (7)$$

so that the ion is displaced from the origin and thus has a dipole moment. If the ion is singly charged, the dipole moment $\mu = e|x_0| = e(-f_0/g_0)^{1/2}$ and this dipole can orient itself parallel or antiparallel to the X-axis. We shall see that this model always leads to ferroelectricity. It is called the dipole model; it is discussed in the next section. TGS and related compounds seem to be examples of it.

(2) $f_0 > 0$, $g_0 > 0$. In this case V(x) has its minimum value at $x = 0$, so that the origin is a true equilibrium position for the ion. When the interaction with the other ions is taken into account, it may be shown that under certain conditions a spontaneous displacement of the ion can occur, leading again to ferroelectric behavior. This model is therefore called the displacement-type model, and the materials satisfying the above condition are called displacement-type ferroelectrics. They are discussed in Section A.4. $Ba\ Ti\ O_3$, $Li\ Ta\ O_3$ and SBN seem to be examples of it.

3. The Dipole Model

We assume here that the elementary cells in the material can be polarized parallel or antiparallel to the local electric field E_ℓ and that they have a permanent dipole moment μ. The local field E_ℓ acting on this elementary dipole is

$$E_\ell = E + \frac{\lambda P}{\varepsilon_0} \tag{8}$$

where E is the applied field, P the polarization and λ the Lorentz factor.

In complete analogy with the magnetic case, it can be shown that the net polarization P for N elementary dipoles per unit volume is

$$P = N\mu \tanh\left(\frac{\mu E_\ell}{kT}\right) \tag{9}$$

If one now puts $E = 0$, one finds that there is a temperature T_C so that Eq. (9) has a non-zero solution for P if $T < T_C$. In other words the material is ferroelectric for $T < T_C$, and T_C is the Curie temperature of the material.

We now invert Eq. (9) and substitute for E_ℓ. This yields after a Taylor expansion of the $\tanh^{-1}$ term

$$(E + \frac{\lambda P}{\varepsilon_0}) = \frac{kT}{\mu^2 N} P + \frac{kT}{3\mu^4 N^3} P^3 + \ldots.$$

$$\text{or} \quad E = (\frac{kT}{\mu^2 N} - \frac{\lambda P}{\varepsilon_0}) P + \frac{kT_C}{3\mu^4 N^3} P^3 + \ldots. \tag{10}$$

where we have replaced T by T_C in the last term. Comparing Eq. (10) with Eq. (1) we see that

$$\beta = \frac{k}{\mu^2 N} \;;\quad B = \frac{kT_C}{3\mu^4 N^3} \;;\quad T_C = \frac{\lambda}{\varepsilon_0} \frac{\mu^2 N}{k} \tag{10a}$$

so that

$$\frac{P}{(\varepsilon - 1)^{1/2}} = (\frac{3}{2} \varepsilon_0 \frac{Nk}{T_C})^{1/2} \tag{11}$$

We now see that the density of dipoles may be written

$$N = \frac{A_0 \rho}{nW} \tag{12}$$

where A_0 is Avogadro's number, ρ is the density, W the molecular weight, and n is the number of molecules per unit cell (this takes into account the possibility of more than one molecule per unit cell.) This yields

$$\frac{P}{(\varepsilon - 1)^{1/2}} = 10.5 \times 10^{-9} \left(\frac{\rho}{n \frac{W}{100} \frac{T_C}{1000}} \right)^{1/2} \text{Coulomb cm}^{-2}\ {}^\circ\text{K}^{-1} \tag{13}$$

This usually lies between (3 - 8) x 10^{-9} Coulomb cm^{-2} $°\text{K}^{-1}$ whereas the experimental value for most materials lies around 3 x 10^{-9} Coulomb cm^{-2} $°\text{K}^{-1}$. For TGS near the Curie temperature, for which the model should especially apply, the agreement is even closer. In view of the rather crude model, this is very good agreement.

This theory was published in Ferroelectrics: J. H. Judy, H. D. Park and A. van der Ziel, The Molecular Field Model Applied to Pyroelectric Detectors, Ferroelectrics, 8, 685-687, 1974.

4. The Displacement-Type Model

We start with the potential energy of the ion

$$V(x) = \frac{1}{2} f_0 x^2 + \frac{1}{4} g_0 x^4 \qquad (14)$$

The equations of motion of the ion may then be written, if the ion is assumed to be singly charged, as

$$m\ddot{x} + f_0 x + g_0 x^3 = e\,E_\ell \qquad (15)$$

where m is the mass of the ion and E_ℓ the local field.

The thermal, incoherent, anharmonic oscillation of the ions is the solution of the homogeneous equation

$$m\ddot{x} + f_0 x + g_0 x^3 = 0 \qquad (15a)$$

with the solution

$$x = \sum_n x_n \cos n\,\omega_0 t \qquad \omega_0 = \frac{f_0}{m} \qquad (16)$$

We must now solve Eq. (15) under the presence of these oscillations. To that end we write

$$x = \sum_n x_n \cos m\omega_0 t + y_1 \qquad (16)$$

and average over a complete cycle. We then obtain

$$m\ddot{y}_1 + [f_0 + 3g_0\overline{(\sum_n x_n \cos n\omega_0 t)^2}]y_1 + g_0 y_1{}^3 = eE_\ell$$

or

$$m\ddot{y}_1 + fy_1 + gy_1 = eE_\ell \qquad (17)$$

because all other terms disappear in the averaging process. Here

$$f = f_0 + \frac{3g_0kT}{f_0} \quad ; \quad g = g_0 \tag{17a}$$

since, according to the equapartition law

$$\overline{(\sum_n x_n \cos n\, \omega_0 t)^2} \simeq \frac{kT}{f_0}$$

as long as the anharmonicity is not too large.

We shall now try to find out whether there is a case for which all ions are displaced over the same distance y_1. If that is so, we may write

$$E_\ell = E + \frac{\gamma P}{\varepsilon_0} = E + \frac{\gamma e N y_1}{\varepsilon_0} \tag{18}$$

Substituting into (17) this yields

$$m\ddot{y}_1 + (f - \frac{e^2 N\gamma}{\varepsilon_0})\, y_1 + g_0 y_1{}^3 = eE \tag{19}$$

If a temperature T_C can be found such that

$$f(T_C) = f_0 + \frac{3g_0kT_C}{f_0} = \frac{e^2N\gamma}{\varepsilon_0} \tag{19a}$$

then the material is ferroelectric for $T < T_C$ and paraelectric for $T > T_C$. The necessary and sufficient condition for this is

$$f_0 < \frac{e^2N\gamma}{\varepsilon_0} \tag{19b}$$

and then

$$T_C = \frac{(e^2N\gamma/\varepsilon_0 - f_0)f_0}{3g_0k} \tag{19c}$$

For $f_0 > e^2N\gamma/\varepsilon_0$ the material is always paraelectric.

If condition (19b) is satisfied, Eq. (19) has a non-zero, steady state solution for $E = 0$, because

$$(f - \frac{e^2N\gamma}{\varepsilon_0})y_1 + g_0y_1{}^3 = 0$$

has the solution

$$y_1 = y_{10} = \left(\frac{e^2N\gamma/\varepsilon_0 - f_0}{g_0}\right)^{1/2} = \left[\frac{3k(T_C - T)}{f_0}\right]^{1/2} \qquad (20)$$

so that the spontaneous polarization P_S is

$$P_S = eNx_{10} = eN\left(\frac{3k}{f_0}\right)^{1/2} (T_C - T)^{1/2} \qquad (20a)$$

and the pyroelectric coefficient p is

$$p = -\frac{dP_S}{dT} = \frac{eN}{2}\left(\frac{3k}{f_0}\right)^{1/2} \frac{1}{(T_C - T)^{1/2}} \qquad (20b)$$

To find the dielectric constant ε, we apply a small d.c. field E, so that $y_1 = y_{10} + \Delta y$. Neglecting higher order terms in Δy, Eq. (19) yields

$$\Delta y\left(f + \frac{e^2N\gamma}{\varepsilon_0} + 3g_0\, y_{10}{}^2\right) = eE$$

or

$$\Delta y = eE\,\frac{f_0}{6g_0K(T_C - T)} \qquad (21)$$

and $\Delta P = eN\Delta y = e^2N\,\dfrac{f_0}{6g_0k(T_C - T)}\,E = \dfrac{e^2NT_C}{2(T_C - T)(e^2N\gamma/\varepsilon_0 - f_0)}\,E$ (21a)

so that $\varepsilon - 1 = \dfrac{\Delta P}{\varepsilon_0 E} = \dfrac{e^2N}{\varepsilon_0}\,\dfrac{T_C}{2(T_C - T)(e^2N\gamma/\varepsilon_0 - f_0)}$ (21b)

and hence the figure of merit of the material is

$$\frac{p}{(\varepsilon - 1)^{1/2}} = \left(\frac{3\varepsilon_0 Nk}{2T_C}\right)^{1/2}\left(\frac{e^2N\gamma/\varepsilon_0 - f_0}{f_0}\right)^{1/2} \qquad (22)$$

The first term in (22) corresponds to the expression found for the dipole model; if the factor

$$\left(\frac{e^2N\gamma/\varepsilon_0 - f_0}{f_0}\right)^{1/2} \qquad (22a)$$

does not differ too much from unity the two models give approximately the same result. It again makes values of the order of 3.0×10^{-9} Coulomb cm^{-2} $°K^{-1}$ for $p/\varepsilon^{1/2}$ understandable.

In analogy with the thermodynamical model one might expect that higher order terms in $V(x)$ would give rise to a significant temperature dependence of $p/\varepsilon^{1/2}$. However this has not been worked out in detail.

This paper is being published in one of the forthcoming issues of Ferroelectrics:

H. D. Park, A. van der Ziel and J. H. Judy, $p/(\varepsilon - 1)^{1/2}$ for Displacement Type Ferroelectrics, Ferroelectrics, in the press.

The work contained in Section A has appeared in greater detail in Mr. H. D. Park's Ph.D. thesis.

B. Other Theoretical and Experimental Work on Ferroelectrics and Dielectrics

1. Feedback Theory of Ferroelectricity

We establish here an analogy between the theory of ferroelectricity and feedback theory.

Let there be N polarizable atoms per unit volume in a dielectric, each having a polarizability α, then the polarization P is

$$P = N\alpha E_\ell = N\alpha(E + \frac{\gamma P}{\varepsilon_0}) \quad ; \tag{23}$$

where E_ℓ is the local field, E the applied field and γ the Lorentz factor. Solving for P yields for the susceptibility

$$\varepsilon - 1 = \frac{P}{\varepsilon_0 E} = \frac{N\alpha/\varepsilon_0}{1 - \gamma N\alpha/\varepsilon_0} \tag{24}$$

corresponding to the gain of a feedback amplifier with a gain $N\alpha/\varepsilon_0$ for zero feedback and feedback factor γ.

If $\gamma N\alpha/\varepsilon_0 < 1$ at all temperatures, the material is a normal dielectric; if $\gamma N\alpha/\varepsilon_0 > 1$ for some temperature range, then the material has spontaneous polarization, or is ferroelectric, in that temperature range. These criteria correspond to the Nyquist condition in feedback amplifiers.

In the ferroelectric regime there is polarization at zero applied field. According to (23) this is only possible if α is a function of P as well as of the absolute temperature T, such that

$$\frac{\gamma N\alpha(T,P)}{\varepsilon_0} \equiv 1 \tag{25}$$

in that temperature range. This means that $\alpha(T,P)$ decreases with increasing $|P|$ and that $|P|$ adjust itself such that (25) is satisfied; it also means that $\alpha(T,P)$ must be a function of P^2. Equation

(25) is equivalent to the Nyquist condition for a stable amplitude in oscillators.

For most ferroelectric materials there is spontaneous polarization P_S below the Curie temperature T_C and $P_S = 0$ at $T = T_C$. The Curie temperature is then given by

$$\frac{\gamma N \alpha_0 (T_C)}{\varepsilon_0} = 1 \tag{26}$$

when $\alpha_0(T_C)$ is the value of $\alpha(T,P)$ for $P = 0$. Corresponding to the limit of stability in feedback amplifiers.

In analogy with the feedback amplifier we may write

$$\alpha(T,P) = \frac{\alpha_0(T)}{1 + BP^2 + CP^4 + \ldots.} \tag{27}$$

Substituting into (23) and solving for the field E yields

$$E = \frac{1 - \gamma N \alpha_0(T)/\varepsilon_0}{N\alpha_0(T)} P + \frac{B}{N\alpha_0(T)} P^3 + \frac{C}{N\alpha_0(T)} P^5 + \ldots. \tag{27a}$$

which corresponds to the thermodynamical theory of ferroelectricity. That theory thus corresponds to what would be expected from feedback considerations.

Since the thermodynamical theory has now been established, one can calculate $\varepsilon - 1$ and the pyroelectric coefficient p, near the Curie temperature and one can evaluate $p/(\varepsilon - 1)^{1/2}$. It is also easy to show that $\alpha_0(T)$ must decrease with increasing T for T near T_C.

This work is scheduled to be published in one of the forthcoming issues of Ferroelectrics:

A. van der Ziel, J. H. Judy and H. D. Park, Feedback Theory of Ferroelectricity, Ferroelectrics 9, 1975, in the press.

2. Solar Power Generation with the Pyroelectric Effect

This work was performed while at the University of Florida and only the publication costs were charged to the contract.

As is well known, when an incoming power density P is chopped at the rate f/sec and $P_1 \exp(j\omega\tau)$ is the power density of frequency ω then the current amplitude is

$$I_{d0} = \frac{\eta A p P_1}{cd(1 + 1/j\omega\tau_H)} \tag{28}$$

where $\omega = 2\pi f$, η is the emissivity of the front face, p the dielectric coefficient, c the specific heat capacity per unit volume, A the device area, d the device thickness and τ_H the heat time constant of the system

$$\tau_H = \frac{cd}{(\eta + \eta')4\sigma T^3} \tag{28a}$$

where η' is the emissivity of the back face, T the absolute temperature of the device and σ the Stefan-Boltzmann constant.

The device has a capacitance $C = \varepsilon\varepsilon_0 A/d$. If a load resistance R is applied, maximum power is transferred if $\omega CR = 1$ and the transferred power is

$$P_{max} = \frac{|I_{do}|^2}{4\omega C} = \frac{\eta^2 p^2 (P_1 A)^2}{4c^2 d^2 [1 + \frac{1}{\omega^2 \tau_H{}^2}] \frac{\omega\varepsilon\varepsilon_0 A}{d}} \tag{29}$$

which has an optimum value P_{opt} if $\omega\tau_H = 1$, so that

$$\frac{P_{opt}}{A} = \frac{\eta^2 p^2 P_1{}^2}{8c(\eta + \eta')4\sigma T^3 \varepsilon\varepsilon_0} \tag{30}$$

The efficiency $\eta_p = \frac{P_{opt}/A}{P}$

turns out to have a very small value. This is not so surprising for the device is essentially a high impedance device; it gives a large voltage but only a small power. Nevertheless it was thought worth while to put it on record; to our surprise it gained a lot of interest.

This work was published in the Journal of Applied Physics: A. van der Ziel, Solar Power Generation by the Pyroelectric Effect, J. Appl. Phys., 45, 4128, Sept. 1974.

3. Equivalent Circuit and Equipartition Theorem in Dielectrics

At high frequencies the dielectric constant ε becomes complex and its absolute value is less than the low-frequency value ε_s. It was shown that for a dielectric without low-frequency losses the susceptibility may be written

$$\varepsilon - 1 = \frac{\varepsilon_s - 1}{1 + j\omega\tau} \qquad (31)$$

where τ is the time constant of the dielectric, so that the admittance of the capacitor is

$$Y = j\omega\varepsilon\varepsilon_0 \frac{A}{d} = j\omega\varepsilon_0 \frac{A}{d} + \frac{j\omega\varepsilon_0(\varepsilon_s - 1)A}{d(1 + j\omega\tau)} \qquad (32)$$

This leads to the equivalent circuit of Fig. 1a, with

$$C_0 = \frac{\varepsilon_0 A}{d} ; \; C_{ps} = \frac{\varepsilon_0(\varepsilon_s - 1)A}{d} ; \; R_{ps} = \frac{\tau d}{\varepsilon_0(\varepsilon_s - 1)A} \qquad (32a)$$

The resistance R_{ps} shows, of course, thermal noise.

Calculating the mean square output voltage yields

$$\overline{\Delta V_0^2} = \frac{kT}{C_0} \frac{C_{ps}}{C_{ps} + C_0} >> \frac{kT}{C_s} \qquad (33)$$

indicating that the equipartition law does not hold in this case.

This is not, however, what is measured when the capacitor is a pyroelectric capacitor that is part of an array of pyroelectric detectors. Let this array be scanned at the rate f_S, then the lower cut-off frequency of the system f_1 is of the order of f_S and the upper cut-off frequency f_2 is determined by the scanning time of a single element of the array. We must now evaluate the contribution $\overline{d\Delta V_0{}^2}$ to the output voltage between the frequencies f and f + df and integrate over the passband of the system

$$\overline{\Delta V_0{}^2} = \int_{f_1}^{f_2} \overline{d(\Delta V_0{}^2)} \tag{33a}$$

Usually $2\pi f_2 \tau << 1$ and then $\overline{\Delta V_0{}^2}$ is much smaller than kT/C_s. This comes about because in the previous case the main contribution to $\overline{\Delta V_0{}^2}$ came from the very high frequencies to which the system does not respond.

For a dielectric with low-frequency losses it was shown that the susceptibility may be written

$$\varepsilon - 1 = \frac{\varepsilon_\infty - 1}{1 + j\omega\tau} + \frac{\varepsilon_s - \varepsilon_\infty}{1 + j\omega\tau_1} \qquad (\tau_1 >> \tau) \tag{34}$$

where $\varepsilon_s - 1$ is the low frequency susceptibility ($\omega\tau_1 << 1$) and $\varepsilon_\infty - 1$ is the high-frequency susceptibility ($1/\tau_1 << \omega << 1/\tau$). This expression is reasonably accurate if the low frequency losses with the relatively long time constant τ_1 are not too large ($\varepsilon_s - \varepsilon_\infty << \varepsilon_\infty - 1$).

The device admittance is in this case

$$Y = \frac{j\omega\varepsilon_0 A}{d} + \frac{j\omega(\varepsilon_\infty - 1)\varepsilon_0 A}{d(1 + j\omega\tau)} + \frac{j\omega(\varepsilon_s - \varepsilon_\infty)\varepsilon_0 A}{d(1 + j\omega\tau_1)} \tag{35}$$

This can be represented by the equivalent circuit of Fig. 1b where

$$\left.\begin{aligned} C_0 &= \frac{\varepsilon_0 A}{d} \; ; \; C_{p\infty} = \frac{\varepsilon_0(\varepsilon_\infty - 1)A}{d} \; ; \; R_{p\infty} = \frac{\tau d}{\varepsilon_0(\varepsilon_\infty - 1)A} \\ C_1 &= \frac{\varepsilon_0(\varepsilon_s - \varepsilon_\infty)A}{d} \; ; \; R_1 = \frac{\tau_1 d}{\varepsilon_0(\varepsilon_s - \varepsilon_\infty)A} \end{aligned}\right\} \tag{35a}$$

The resistors R_1 and $R_{p\infty}$ show, of course, thermal noise.

If one calculates the contribution to $\overline{\Delta V_0^2}$ due to the thermal noise of R_1, and one neglects $R_{p\infty}$, one obtains

$$\overline{\Delta V_0^2} = \frac{kT}{C_s} \frac{\varepsilon_s - \varepsilon_\infty}{\varepsilon_\infty} \tag{36}$$

This is much less than the equipartition law would indicate, and the contribution of the dielectric losses to the output voltage in a pyroelectric array would be correspondingly small.

We can also put the latter as follows. Normally one characterizes the device by its capacitance C and the losses by the loss tangent tanδ. Over the limited range of frequencies usually used in arrays C and tanδ are practically constant. Therefore the open circuit device voltage has a spectrum

$$S_V(f) = 4kT \frac{\tan\delta}{\omega C} \tag{37}$$

so that the mean square output voltage is

$$\overline{\Delta V_{eff}^2} = \int_{f_1}^{f_2} S_V(f)df = \frac{2}{\pi} \frac{kT}{C} \ln(\frac{f_2}{f_1}) \tan\delta \tag{37a}$$

This can be much less than kT/C, the value given by the equipartition law.

This work was published in the Journal of Applied Physics:

A. van der Ziel, Equivalent Circuit and Equipartition Theorem in Ideal Dielectric and Ferroelectric Capacitors, J. A. P. 45, 1400-1401, March 1973.

A. van der Ziel, Equivalent Circuit and Equipartition Theorem in Lossy Dielectric and Ferroelectric Capacitors, J. A. P. 45, 1402-1403, March 1973.

4. Partition Noise as the Cause of Thermal Noise in a Two-Level Ferroelectric

In a two-level ferroelectric the dipole moment can orient itself parallel or antiparallel to the local electric field $E_\ell = E + \gamma P/\varepsilon_0$, E being the applied field, P the polarization and γ the Lorentz factor. Let N be the density of dipoles and let N_1 be parallel to the field and N_2 be antiparallel to the field so that $N_1 + N_2 = N$. The polarization

$$P = \mu(N_1 - N_2) \quad ; \quad \Delta P = 2\mu\Delta N_1 \tag{38}$$

since $\Delta N_2 = - \Delta N_1$. Let N_{10} and N_{20} be the equilibrium values of N_1 and N_2.

Now according to the theory of polarization noise the polarization noise spectrum is given by

$$S_{\Delta p}(f) = \frac{4kT\varepsilon_0(\varepsilon_s - 1)}{V\tau} \quad \frac{\tau^2}{1 + \omega^2\tau^2} \tag{39}$$

(Nyquist equivalent) where ε_s is the low frequency dielectric constant, τ the macroscopic time constant of the dielectric and V the volume of the sample. Working backwards, it is shown that the fluctuation $\overline{\Delta N_1{}^2}$, without the feedback caused by the dependence of the local field upon the polarization, is given by

$$\overline{\Delta N_1{}^2} = \frac{N_{10}N_{20}}{N_{10} + N_{20}} \frac{1}{V} \tag{40}$$

which is just the partition noise expected for the two-level system. The conclusion is therefore that the thermal noise in this case is caused by the partition noise of the two level system.

This work was published in Ferroelectrics:

A. van der Ziel, H. D. Park and J. H. Judy, Partition Noise as the Cause of Thermal Noise in a Two-Level Ferroelectric, Ferroelectrics, 8, 689-690, 1974.

5. Polarization Fluctuations in Capacitive Bolometers

A capacitive bolometer uses a ferroelectric operating slightly above the Curie temperature. Modulated radiation incident upon the bolometer gives rise to a fluctuating temperature and hence a fluctuating capacitance, and this fluctuating capacitance is detected by applying a d.c. voltage V to the capacitor, corresponding to an applied field $E = V/d$.

At zero field the noise resistance R_n of the open-circuit capacitance C was equal to the series resistance $R_s = \tan\delta/(\omega C)$ where ω is the angular frequency and $\tan\delta$ the loss tangent of the material, but at high fields $R_n > R_s$ and R_n saturated at high fields. There is presently no satisfactory explanation for this phenomenon.

This work was published in the Journal of Applied Physics: V. P. Singh and A. van der Ziel, Polarization Fluctuations in Capacitive Bolometers, J. A. P. 45, 1452-1453, March 1974.

6. Limiting Flicker Noise in MOSFETs

It is very tempting to use MOSFETs in pyroelectric arrays, since they are more easily integrated into the system. Single pyroelectric detectors usually use JFETs since they give lower noise. It is therefore important to point out that MOSFETs are inherently noisier than JFETs.

The reason is a very simple one. The gate-oxide-semiconductor capacitance C has a loss tangent $\tan\delta$ and hence a series resistance $R_s = \tan\delta/(\omega C)$ that shows thermal noise. The limiting noise resistance R_n of a MOSFET is therefore

$$R_n = R_s = \frac{\tan\delta}{\omega C} \tag{41}$$

If we take $\tan\delta = 10^{-4}$ and $C = 5\text{pF}$, then $R_n = 3 \times 10^6/f$ ohm, corresponding to 3MΩ at 1 Hz. In contrast, good JFETs may have $R_n = 10^4\Omega$ at 1 Hz.

This work is being published in Solid State Electronics: A. van der Ziel, Limiting Flicker Noise in MOSFETs, Solid State Electronics, in the press.

C. The Capacitive Bolometer

1. The D.C. Capacitive Bolometer

For a ferroelectric capacitor operating slightly above the Curie temperature T_C, the material is paraelectric and the capacitance is

$$C = \frac{\text{const}}{T - T_C} \tag{42}$$

Modulated radiation of frequency ω produces a variation in capacitance, this variation is detected by applying a d.c. voltage V_0 in series with the capacitor and connecting the circuit to a large load resistance R such that $\omega C_0 R >> 1$, where C_0 is the equilibrium value of C.

The heat response of the detector due to the incident radiation $P_1 \exp(j\omega t)$ is given by

$$C_H \frac{d\Delta T}{dt} + (g_H + g_H')\Delta T = \eta P_1 \exp(j\omega t) \tag{43}$$

where the heat capacitance $C_H = cAd$, where c is the specific heat per cm^3, A the device area and d the device thickness, η is the emissivity of the front face, g_H and g_H' are the heat loss conductances of the front and back face and ΔT is the temperature change due to the incident radiation.

Putting $\Delta T = \Delta T_0 \exp(j\omega t)$ and solving for ΔT_0 yields

$$\Delta T_0 = \frac{\eta P_1}{j\omega C_H[1 + 1/(j\omega\tau_H)]} \tag{44}$$

where $\tau_H = C_H/(g_H + g_H')$ is the thermal time constant of the system. Since $\tau_H \simeq 1$ sec and $\omega \simeq 10 - 100$ per sec., $\omega^2\tau_H^2 >> 1$, so that

$$\Delta T_0 \simeq \frac{P_1}{j\omega C_H} = \frac{P_1}{j\omega cAd} \tag{44a}$$

The capacitance may therefore be written

$$C = C_0 + \frac{\partial C_0}{\partial T} \Delta T_0 \exp(j\omega t) \qquad (45)$$

If the capacitance is reasonably linear with respect to the applied voltage, the charge Q of the capacitor is CV_0 and the short-circuit current is

$$I = \frac{dQ}{dt} = V_0 \frac{dC}{dt} = j\omega V_0 \frac{\partial C_0}{\partial T} \Delta T_0 \exp(j\omega t) \qquad (46)$$

Hence the output voltage $v_0 \exp(j\omega t)$ has an amplitude

$$v_0 = \frac{j\omega V_0 (\partial C_0/\partial T)\Delta T_0}{j\omega C_0} = V_0 \frac{1}{C_0} \frac{\partial C_0}{\partial T} \Delta T_0 = - \frac{\eta P_1 E_0}{j\omega c A(T - T_C)} \qquad (47)$$

where $E_0 = V_0/d$, so that the output voltage is proportional to the d.c. field E_0. For large field saturation effects will set in that will be discussed in a moment.

Assuming the noise of the device to be thermal noise of the dielectric losses

$$S_V(f) = \frac{4kT \tan\delta}{\omega C_0} = \frac{4kT \tan\delta\ d}{\omega \varepsilon \varepsilon_0 A} \qquad (48)$$

Defining the noise equivalent power P_{eq} by

$$(V_0)_{rms} = [S_V(f)]^{1/2}$$

yields

$$P_{eq} = \frac{c(T - T_c)}{\eta E_0} \left(\frac{4kT \tan\delta}{\varepsilon\varepsilon_0}\right)^{1/2} (\omega A d)^{1/2} \qquad (49)$$

Since ε varies as $(T - T_c)^{-1/2}$, P_{eq} varies as $(T - T_c)^{3/2}$. The lowest P_{eq} is thus obtained by keeping the temperature as close to the Curie temperature as possible.

When saturation effects set in, one must use the charge $Q = AP(V_0,T)$ directly, where $P(V_0,T)$ is the induced polarization. The current is therefore

$$I(t) = I_{d0} \exp(j\omega t) = j\omega A \frac{\partial P}{\partial T} \Delta T_0 \exp(j\omega t) \qquad (50)$$

and the output voltage has an amplitude

$$v_0 = \frac{I_{d0}}{j\omega C_0} = \frac{A}{C_0} \frac{\partial P}{\partial T} \Delta T_0 = \frac{1}{C_0} \frac{\partial Q}{\partial T} \Delta T_0 \quad (51)$$

where

$$C_0 = \frac{\partial Q}{\partial V_0} = A \frac{\partial P}{\partial V_0} \quad (52)$$

We now introduce the d.c. capacitance $C_d = Q/V_0$, so that $Q = C_d V_0$. Hence

$$v_0 = V_0 \frac{1}{C_0} \frac{\partial C_d}{\partial T} \Delta T_0 \quad (53)$$

Eq. (47) must now be replaced by (53), i.e. $\partial C_0/\partial T$ must be replaced by $\partial C_d/\partial T$. Saturation means that the factor

$$V_0 \frac{1}{C_0} \frac{\partial C_d}{\partial T}$$

saturates.

At large fields the noise is somewhat larger than the thermal noise of the dielectric losses. P_{eq}, as given by (49), is thus somewhat too optimistic.

Experimental results are discussed in Section C3.

2. The A.C. Capacitive Bolometer

In the a.c. biased bolometer an a.c. signal $V_0 \cos \omega_0 t$ is applied to the bolometer, where $\omega_0 >>$ the frequency ω of the incident radiation, and series tunes the circuit by an inductance L connected between the a.c. signal and the bolometer. If C_0 is the quiescent capacitance of the bolometer this means that $\omega_0{}^2 L C_0 = 1$. The output signal is taken from the capacitor.

We can now calculate the response and find that it is the same as for the d.c. case, except that the incident radiation produces two sidebands of frequencies $\omega_0 - \omega$ and $\omega_0 + \omega$, that can be detected by a linear detector. The noise emf per unit bandwidth is series with the capacitance now has a spectrum

$$S_V(f) = (4kT \frac{\tan\delta}{\omega_0 C_0}) \qquad (54)$$

Consequently if one calculates P_{eq}, one finds

$$(P_{eq})_{a.c.} = (P_{eq})_{d.c.} (\frac{\omega}{\omega_0})^{1/2} \qquad (55)$$

For $\omega/\omega = 1000$ the a.c. value of P_{eq} is thus 30 times smaller than the d.c. value, indicating the great advantage of the a.c. bolometer.

This scheme has not been tried in practice. There are some difficulties to be overcome; for example the capacitance C not only varies in the rhythm of the signal of frequency ω but also in the rhythm of the signal of frequency ω_0. It would be worth while, however, to try it out in practice and see what can be achieved.

3. Experimental Results for the D.C. Bolometer

In his Ph.D. thesis, Dr. Singh has given extensive measurements of the capacitive bolometer effect in TGS. He finds that the sensitivity in V/W is linear to the d.c. field E_0 at low fields but saturates for fields higher than 10kV. Closer to the Curie temperature saturation effects set in earlier. He also finds that the inverse of the sensitivity varies linearly with $T - T_C$, as expected from Eq. (47). He has also measured the effect of the d.c. field on the small-signal capacitance. He compared the series resistance R_s and the noise resistance R_n of the device and found $R_n > R_s$ at high d.c. fields.

Finally, he has compared the operation of sample TGS 42, which had a Curie temperature of 49.8°C, as a capacitive bolometer at 52.7°C and as a pyroelectric detector at room temperature. He found in the first case a maximum noise equivalent however $P_{eq} = 1.26 \times 10^{-9}$ W/Hz$^{1/2}$ at a field of 9kV, whereas the same device, when used as a pyroelectric detector at room temperature had $P_{eq} = 1.71 \times 10^{-9}W/Hz^{1/2}$. Since operation closer to the Curie temperature would have been feasible, and this would have resulted in a lower P_{eq}, it may be concluded that the capacitive bolometer is intrinsically able to compete with the pyroelectric detector.

Dr. Singh also compared the value of $P_{eq} = 1.26 \times 10^{-9}$ W/Hz$^{1/2}$ with the theory as presented by Eq. (49). He obtained a theoretical value for P_{eq} that was about a factor 8 smaller. This factor comes from two reasons

a) Saturation effects reduce the sensitivity at high fields from the value calculated by Eq. (47).

b) At high fields the noise resistance R_n is considerably larger than the series resistance R_s of the device, and this means that Eq. (49) must be multiplied by the factor $(R_n/R_s)^{1/2}$.

Both factors together can probably explain the data.

The details of this work are presented in the following thesis: Vijay Pal Singh, Noise in Ferroelectric Detectors for Infrared Radiation, E. E. Department, University of Minnesota, December 1973.

D. Other Work Performed Under the Contract

1. Diffusion Theory of the Response of Pyroelectric Detectors

In a series of two papers the response of pyroelectric detectors was discussed as an application of the diffusion theory for heat flow. The response was expressed in terms of hyperbolic functions, which greatly simplifies the notation and makes it possible to understand the frequency response almost by inspection.

In the first paper, co-authored with S. T. Liu, the theory was applied to a single free-bearing detector. At very low and very high frequencies the results agree with the elementary lumped circuit approach to the heat problem; at intermediate frequencies the new result improves on the lumped circuit model.

In the second paper the theory was applied to thin pyroelectric films on a substrate and the response was calculated as a function of the substrate and film thickness. It was found that for low-frequency applications, the pyroelectric layer should not be made too thin, preferably several micrometers thick, that the substrate should be as thin as possible and that the product of its specific heat per gram, its density in grams/cm^3 and its heat conductivity should be as small as possible. For thick substrates there is an intermediate frequency region where the value of D* is practically independent of frequency. This intermediate frequency region extends to higher frequencies if the pyroelectric layer is made thinner, but D* decreases with decreasing film thickness in that region. The second study was made in support of our sputtered thin film program. These papers were published in the Journal of Applied Physics:

1. A. van der Ziel and S. T. Liu, Diffusion Theory of the Response of Pyroelectric Detectors, J. A. P., <u>43</u>, 4260, 1972.

2. A. van der Ziel, The Pyroelectric Response and D* of Thin Pyroelectric Films on a Substrate, J. A. P. 45, 546-549, 1973.

2. Thin Film Program (Dr. Wehner)

Films (0.1 - 8μ meter thick) of lead-zirconium-titanate oxide were prepared by RF sputtering in pure Ar and a 10% O_2 in Ar mixture. Substrates of glass, glazed alumina, mica and fused quartz were heated to 500°C during deposition. The film deposited in pure Ar became dark grey whereas those prepared in the 10% O_2 mixture were yellow but quite transparent. Capacitance measurements versus temperature indicated a Curie temperature of about 160°C. Auger spectroscopy studies indicated that the thin film had less Pb than the bulk (about 30%).

PLZT (8% La, 65% Zr, 35% Ti) were sputtered as thin layers (0.1 - 0.5 μ meter thick) on fused quartz and mica substrates in a pure Argon RF triode system. The substrate temperature was varied from 20°C to 500°C. Auger spectroscopy studies indicated that the films were deficient in La and Zr to the extent of about 45% less than the target composition. The films appeared to be ferroelectric, as capacitance measurements indicated.

The studies indicated in general that while it is possible to deposit layers that are ferroelectric, it is not so easy to deposit them with the same composition of the bulk. While such a deposition would be worth while, it will probably require a prolonged effort to make acceptable layers.

3. Materials Program (Dr. Wertz)

The materials program produced a variety of crystals useable as pyroelectric detectors. The most useful crystals were grown crystals of TGS; crystals of rather good quality were obtained in this manner. Later TGS crystals were bought from Isomet.

We also made crystals from pressing powders at high pressure and temperature by the Honeywell Corporation. $BaTiO_3$ and $(Ba,Sr)TiO_3$ crystals were a good example of such a procedure. Other crystals were $Ba(Sn,Ti)O_3$, with a range of compositions of the vicinity of $Ba(Ti_{85},Sn_{0.15})O_3$.

We also made crystals of Tl_3AsSe_3, which has a relatively small gap width, and is a semiconductor rather than an insulator, and the related compound In_3AsSe_3, which was expected to have a larger gap width and would be better at room temperature. None of the crystals were large enough to make good detectors.

We also prepared $Pb_5(Ge,Si)_3O_{11}$ which has a Curie temperature of 84°C. Only small crystals were made by the Crochzalski technique.

Later PLZT and SBN samples became available from Honeywell Corporation and other sources and many devices were made of these materials.

4. Contact Problems

At first we had some serious problems with contacts. Especially with TGS it was very difficult to make good devices with silver or platinum paste. Apparently the solvent attacked the crystal, deteriorated its performance and made the device unstable.

Later very satisfactory results were obtained by vacuum deposition (pressure lower than 10^{-6} Torr). First a thin layer of chronium was evaporated onto one side of the device, followed by a thicker layer of gold. Then the device was turned over and the process repeated on the other side. Thin gold wires were (Sigmund Cohn wire, 1-P) attached to the two electrodes with the help of silver epoxy (Dupont, Silver composition 4922) and the device was mounted. This produced good, stable devices.

Samples that could withstand a much higher temperature, like SBN and PLZT, were first contacted with the help of burned silver or burned gold. Later it was found, however, that better devices could be produced by vacuum deposition of first a thin layer (15Å) of chromium and then a thicker layer (1000Å) of gold. Vacuum deposited gold alone was not satisfactory, since the contacts then deteriorated upon heating; apparently the chromium is needed to make the contact stick better to the material. In this manner very reproducible data could be obtained.

Fig. 2 shows D* versus thickness w for PLZT samples with Cr - Au contacts. Approximately a $D^* = \text{const}\ w^{-1/2}$ relationship was found in agreement with the elementary theory. The measurements were performed at 100 Hz.

Table 1 gives D* measurements for PLZT samples different types of contact. As the table indicates the samples with Cr - Au contacts were the best; the other contacts gave less reproducible results and had in general a lower D*.

Table 1 D* Measurement at 100 Hz

Device no's	Thickness mils	Area 10^{-2} cm^2	Capacitor pf	tanδ	Annealing before worked	Contact	Light Response 10^{-4}, volt rms	Voltage Response v/w	NEP 10^{-9}	D* 10^7
1	2.1	1.51	506	0.074	No	Cr+Au	3.4	36v/w	1.62	7.61
18	2.1	1.51	426	0.026	No	Cr+Au	2.2	24	1.68	7.31
2	3.5	2.48	376	0.039	No	Cr+Au	3.2	22	2.49	6.56
3	4.5	5.23	676	0.052	No	Cr+Au	3.4	11	4.4	5.2
4	4.5	2.48	277	0.02	No	Cr+Au	2.2	14	3.05	5.16
5	4.5	2.48	225	0.015	Yes	Cr+Au	2.6	17	2.58	6.1
7	4.5	2.48	257	0.122	No	Ag Fired 500°C	1.4	91	12.2	0.12
8	4.5	2.48	235	0.08	Yes	"	2.0	13	7.2	2.19
13	4.5		390	0.166	Yes	"				
6	4.5	2.48	212	0.177	No	Au-Fired 800°C	1.2	7.8	16.1	0.98
9	4.5	3.00	372	0.034	No	"	2.0	13	4.8	4.4
10	4.5	2.48	238	0.12	Yes	"	2.0	13	8.82	1.79
11	4.5	2.48	235	0.032	Yes	"	2.2	14	4.09	3.85
12	4.6		721	0.21	Yes	"				
14	11.6	5.23	241	0.04	No	Au-Cr	2.4	7.4	7.74	2.96
15	20.1	5.23	166	0.042	No	Au-Cr	2.4	7.4	8.96	2.56
16	30	5.23	111	0.042	No	Au-Cr	2.4	7.4	0.125	1.83
17	4.5	2.48	204	0.067	No	Silver Paste	1.0	6.5	0.138	1.12

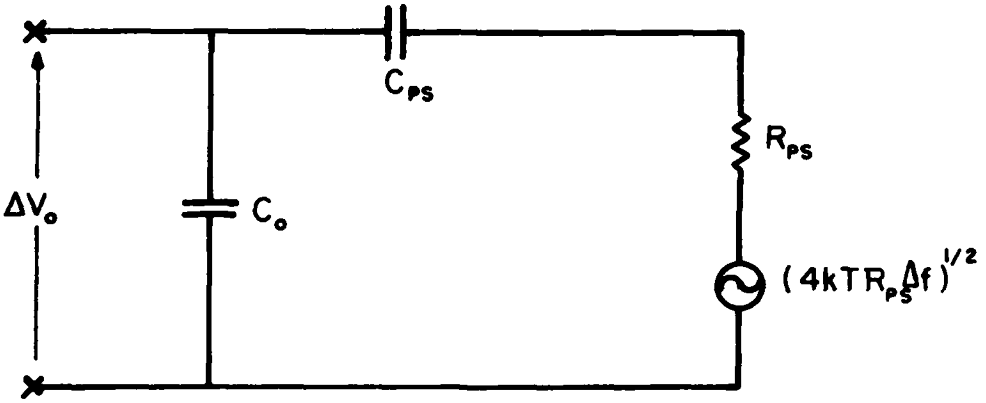

Fig. 1a Equivalent circuit of ideal dielectric

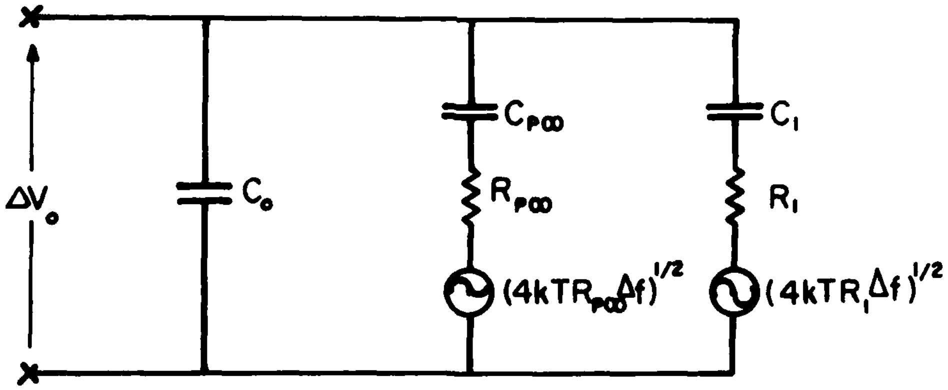

Fig. 1b Equivalent circuit of lossy dielectric

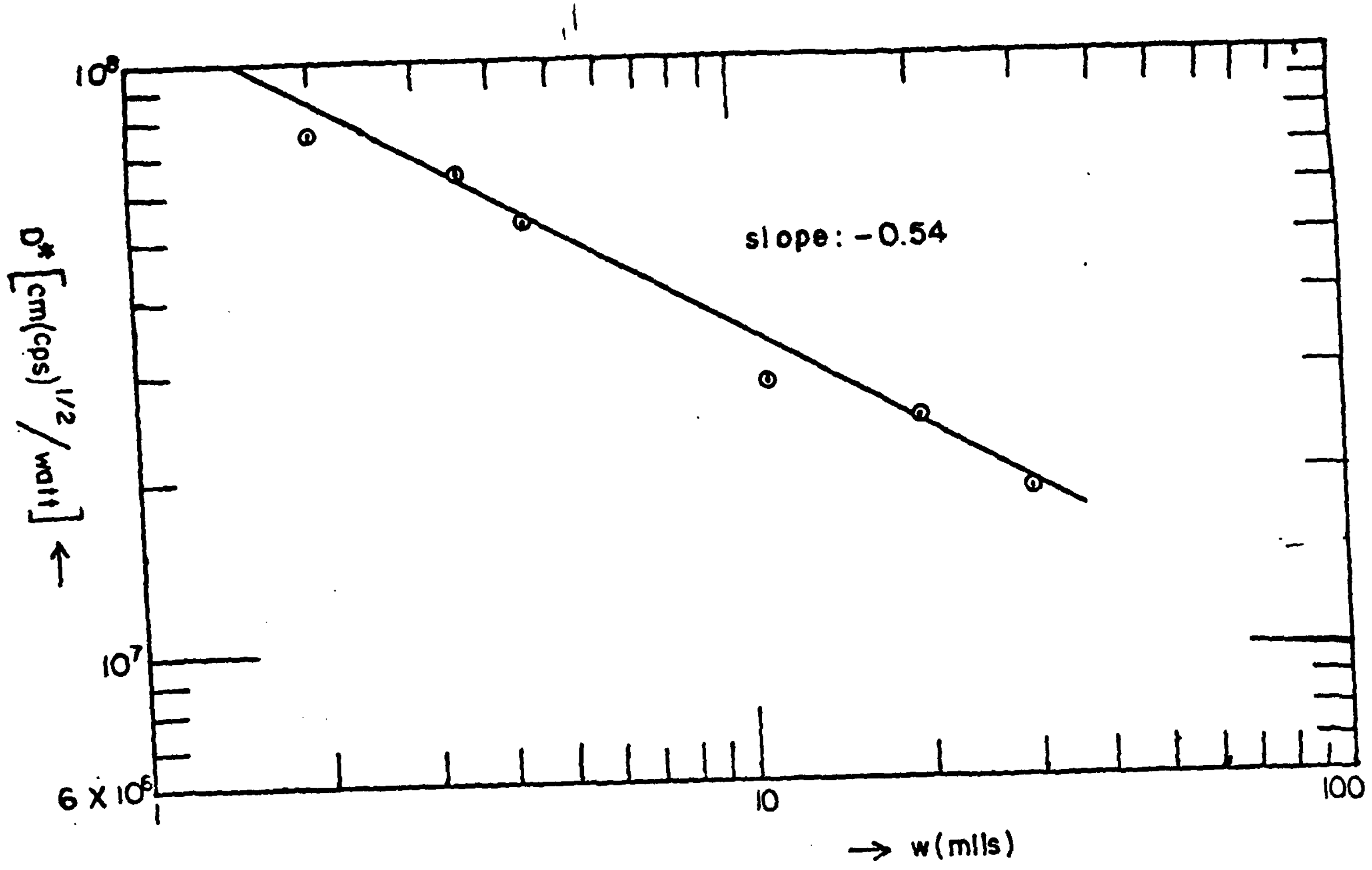

Fig. 2 D* versus w for PLZT samples with Cr-Au contacts

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13. ABSTRACT

This report summarizes work done on the theory of ferroelectric detectors, sources of noise in ferroelectrics and dielectrics, and characteristics and limitations of capacitive bolometers. In addition, results of other work including theory of thermal diffusion in pyroelectric detectors as well as techniques used for material preparation, problems encountered in device fabrication and measurements of D* at 100Hz of PLZT samples are summarized.

The main results are that the parameters of the thermodynamical theory of pyroelectric detectors can be expressed in terms of independent fundamental molecular parameters which yield a lossless material figure of merit $p/\sqrt{\varepsilon}$ in close agreement with experimental valves. This approximate model based on the molecular field approximation predicts that $p/\sqrt{\varepsilon}$ is almost independent of the material parameters over a wide range of pyroelectric materials. Further improvement in detectivity must come from lowering the material loss parameter tanδ. Theoretical work on the noise sources in ferroelectrics led to the conclusion that the thermal noise is caused by the partition noise in a two-level system. A capacitive bolometer operating in the paraelectric region near the Curie temperature exhibited a very low noise equivalent power which is comparable with that of a pyroelectric detector. It is concluded that an understanding of the fundamental loss mechanisms in ferroelectric pyroelectric detectors is needed before improvement in a materials-limited device detectivity can be attained.

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noise equivalent power (NEP)						
specific detectivity (D*)						
responsivity						
capacitive bolometer						
molecular field						
triglycine sulfate (TGS)						

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