Measurement of the pyroelectric coefficient and permittivity from the pyroelectric response to step radiation signals in ferroelectrics

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A method is presented of measuring the pyroelectric coefficient λ and permittivity ϵ from the initial slope, rise time, and peak value of the pyroelectric response to step radiation signals, valid for temperatures up to the Curie point. An experiment carried out on single-crystalline triglycine sulphate has yielded the temperature dependence of λ and ϵ with reasonable accuracy and in good agreement with other methods.

The pyroelectric (PE) coefficient λ $(= dP_s/dT$, P_s being the spontaneous polarization) is of primary importance in the study of the PE effect in ferroelectrics. Chynoweth[1] has developed a dynamic method of measuring λ from the height of the PE current response to pulsed radiation signals, which has been widely used since.[2-6] Some shortages of the method have been discussed and avoided by Lang and Steckel.[7] Here we present a new dynamic method that also puts to work the initial slope, rise time, and fall time of the response. This allows a simultaneous measurement of λ and the permittivity ϵ and may yield the specific heat of the material.

The method is based on a recent analysis by the present authors of the PE voltage response $V(t)$ to step infrared signals.[8] We assumed that the absorbed radiation flux F causes a small temperature rise ΔT that is uniform throughout the PE crystal, and that the thermal capacity C_T of the sample and its thermal conductance to ambient G_T are constant during the signal. The resulting PE charge flow in the circuit of the sample (see Fig. 1) is then described by

$$\frac{d(CV)}{dt} + \frac{V}{R} = A\lambda \frac{d(\Delta T)}{dt} . \tag{1}$$

Here C is composed of the capacitances C_s of the sample and C_t of the preamplifier input, R is the resistance R_s of the sample with the parallel load R_L, and A is the sample area. λ includes both the primary and secondary PE effects; i.e., we assume the sample unclamped and the electric field practically zero. Eq. (1) can be rewritten as

$$C\frac{dV}{dt} + \frac{V}{R}\left(1 + R\frac{dC}{dt}\right) = A\lambda \frac{d(\Delta T)}{dt}. \tag{2}$$

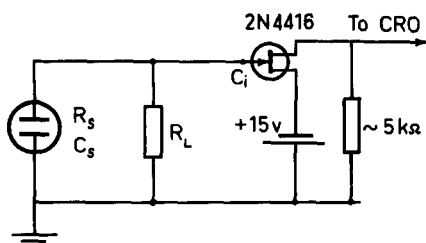For temperatures T far from Curie point T_c, the effect

of dC/dt is negligible, so that

$$C\frac{dV}{dt} + \frac{V}{R} = A\lambda \frac{d(\Delta T)}{dt}. \tag{3}$$

Also, because λ and ϵ can be considered constant during the step signal, we obtained, for a sample with electronic time constant $\tau_e \equiv RC$ smaller than the thermal time constant $\tau_T \equiv C_T/G_T$,

$$V(t) = \xi F\tau_e(1 - \theta)^{-1}[\exp(-t/\tau_T) - \exp(-t/\tau_e)]. \tag{4}$$

Here $\theta \equiv \tau_e/\tau_T$ and ξ is the initial slope k of the response per unit F. When $C_s \gg C_t$, $C \approx C_s$ and ξ is a material constant, $\xi = \lambda/\epsilon_0\epsilon c$, where $\epsilon_0 = 8.85 \times 10^{-12}$ F/m and c is the volume specific heat. For $R_L \ll R_S$, as it is in this experiment, $\tau_e = R_L C_s$.

A PE voltage response, typical under these conditions, is shown by curve I in Fig. 2. At the onset of the step signal, $V(t)$ has an initial slope $k = \xi F$, rises almost exponentially with rise time t_r to a peak value $V_p = k\tau_e\theta^{\theta/(1-\theta)}$, and then decays exponentially with fall time τ_T. We define t_r as the time needed for $V(t)$ to reach $1 - e^{-1} = 63\%$ of V_p, and τ_T is the time constant of the exponential rise of ΔT_s; i.e., $\Delta T = \Delta T_s |1 - \exp(-t/\tau_T)|$, where $\Delta T_s = AF/G_T$. The parameters ϵ
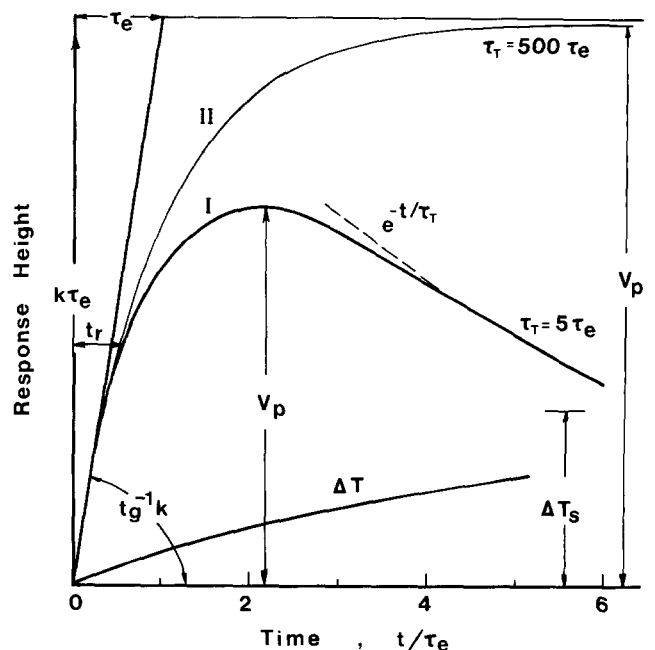

FIG. 1. Measuring circuit.

FIG 2. PE voltage transients for $\theta = 0.2$ (curve I) and $\theta = 0.002$ (curve II).
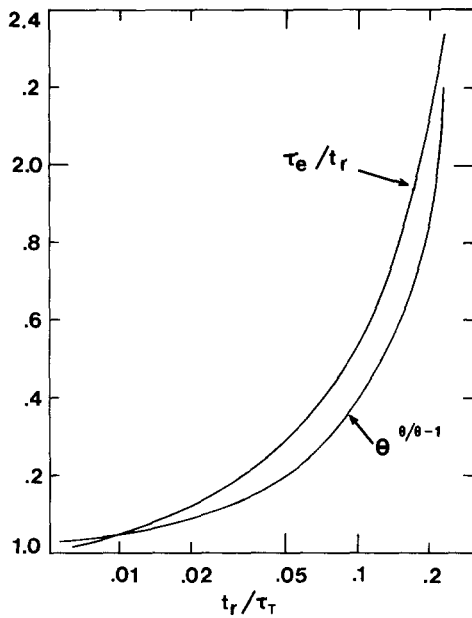
FIG. 3. Computed values of τ_e/t_r and $\theta^{\theta/(\theta-1)}$ vs t_r/τ_T .

and λ can thus be obtained from the parameters of the PE response, using the relations

$$\epsilon = CL/\epsilon_0 A = (L/\epsilon_0 AR_L)\tau_e,$$
$$\lambda = \epsilon_0 \epsilon c \xi = (\epsilon_0 \epsilon c/F)k, \tag{5}$$

where L is the sample thickness. Also, because $k = (V_p/\tau_e)\theta^{\theta/(\theta-1)}$, one obtains a second relation for λ,

$$\lambda = (cL/FAR_L)\theta^{\theta/(\theta-1)}V_p. \tag{5a}$$

The values of τ_e and $\theta^{\theta/(\theta-1)}$, computed from the mea-

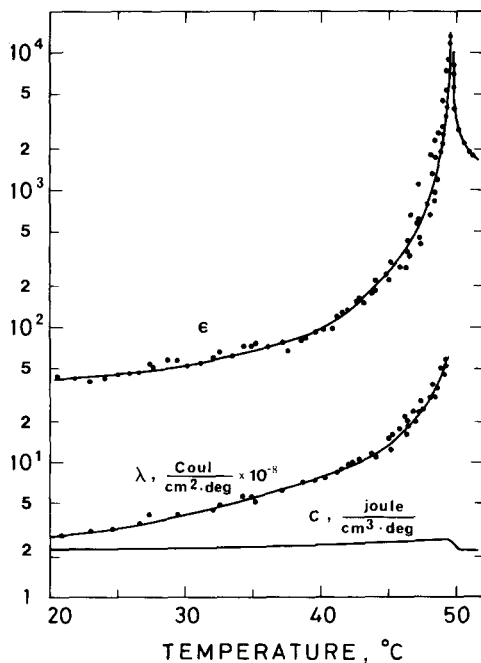sured values of t_r and τ_T, are plotted in Fig. 3. For $\theta \ll 1$ (curve II, Fig. 2), $t_r = \tau_e$ and $V_p = k\tau_e$.

The values of c can be taken from the literature.[9-11] However, a reliable measurement of ΔT_s (which is not presented here) will yield $G_T = AF/\Delta T_s$. From our measurement of τ_T one then has $C_T = AF\tau_T/\Delta T_s$, so that

$$c = (F/L)(\tau_T/\Delta T_s). \tag{6}$$

Let us now consider conditions under which relations (5) and (5a) remain valid for T close to the Curie temperature T_c. The condition that ϵ and λ be constant during the step signal is fulfilled if

$$\Delta T_s \ll T_c - T, \tag{7}$$

because then the increments[11] $\Delta\epsilon \approx \epsilon\Delta T/|T - T_c|$ and $\Delta\lambda \approx \frac{1}{2}\lambda\Delta T/(T_c - T)$ can be disregarded. The effect of dC/dt

FIG. 5. Reciprocal permittivity in three TGS crystals near the Curie temperature: $\triangle$, sample Z-3; $\bigcirc$, sample T-18; $\triangledown$, sample T-24.

FIG. 4. Temperature dependence of measured λ and ϵ for TGS. Values of c according to Refs. 9 and 10.
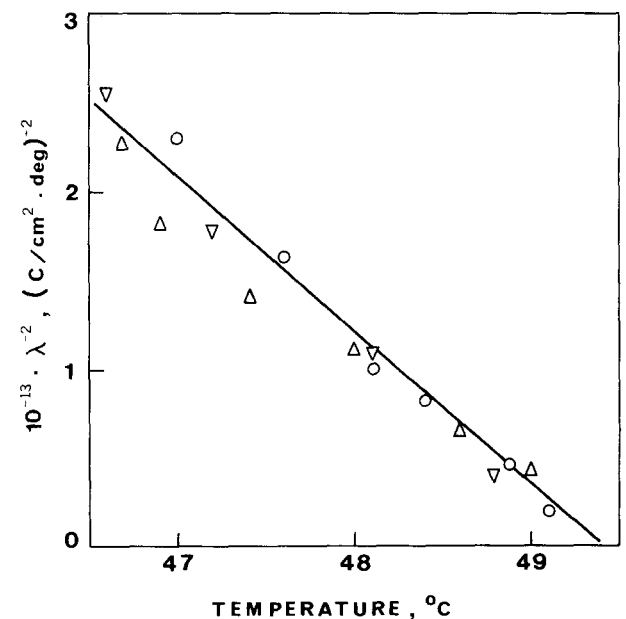

FIG. 6. Squared reciprocal PE coefficient in three TGS crystals near the Curie temperature: $\triangle$, sample Z-3; $\bigcirc$, sample T-18; $\triangle$, sample T-24.

in Eq. (2) is negligible if $R\,dC/dt \ll 1$, or if $(d\epsilon/dt)$ $\times[d(\Delta T)/dt] \ll L/AR$. Because $d(\Delta T)/dt \lesssim \Delta T_s/\tau_T$ and, according to Curie-Weiss law,[11] $d\epsilon/dT = \epsilon(|T - T_c|)^{-1}$, dC/dt can be neglected if

$$\theta \Delta T_s \gg T_c - T. \tag{8}$$

Thus for $\theta < 1$, condition (7) contains (8) and is sufficient for the validity of relations (5) and (5a).

Condition (7) means that one may approach T_c closer, the smaller ΔT_s becomes; e.g., if $\Delta T_s \approx 0.1\,°C$, $T_c - T$ may be $\sim 1\,°C$. Because the rises of C_T and G_T with T are small (compared to those of λ and ϵ), τ_T remains constant in a range considerably closer to T_c. The measurements of λ and ϵ can thus be extended by using R_L small enough to maintain $\theta \ll 1$. Only during the rise of $V(t)$, for $\theta \ll 1$, does one have $\Delta T/\Delta T_s \approx \tau_e/\tau_T$—i.e., $\Delta T \approx \theta \Delta T_s$—and is condition (8) sufficient for the validity of relations (5) and (5a). For example, with $\Delta T_s = 0.1\,°C$ and $\theta = 0.01$, one can approach T_c to $\sim 0.01\,°C$.

Measurements were carried out on six samples, 15—70 μm thick, of single-crystalline triglycine sulphate[12] (TGS) with major faces oriented perpendicular to the PE axis and provided with ir transparent electrodes. The samples were placed in a small oven with a CdS window. The oven was thermistor controlled with a temperature stability better than $0.05\,°C$. The temperature of the sample in the oven was measured within better than $0.1\,°C$ with a calibrated thermocouple attached very close to the rear electrode. The whole mount was held in a vacuum-tight cryostat with a KBr window. The radiation source was a $500\,°K$ blackbody with a shutter fast enough to provide step signals. The PE responses were measured on a Tektronix RM 564 storage cathode-ray oscilloscope (CRO) with a 3A9 amplifier of useable sensitivity at 50 μV/cm and with $R_L = 10^7\,\Omega$ while R_S was $\sim 10^{12}\,\Omega$.

The values of ϵ and λ, obtained from the PE response transients with the use of relations (5) and (5a) are shown in Fig. 4. The c curve in the figure is based on Refs. 9 and 10, and T_c is $\sim 49.5\,°C$. The data of ϵ above T_c are obtained from the small residual PE responses.[13] Figure 5 is a plot of ϵ^{-1} versus T in the vicinity of T_c and shows that the values obtained for ϵ in samples T-18

and T-24 fit the Curie-Weiss law well and yield a Curie constant[11] of $3200\,°K$. A less typical value of $\sim 5000\,°K$ is found in sample Z-3.

The plot of λ^{-2} vs T in the vicinity of T_c is shown in Fig. 6. It fits the thermodynamic theory of a second-order ferroelectric transition[11,14] and has a slope of 8×10^{12} $(C/cm^2\,deg^{1/2})^{-2}$. The agreement between our data and the previously reported experimental and theoretical results shows that the present method can be a useful tool in the study of ferroelectrics. A detailed discussion will be presented together with an analysis of the temperature dependence of the PE voltage response to step infrared signals in ferroelectrics.[15]

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Ageing of the residual surface resistance of superconducting lead cavities

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Measurements of the residual surface resistance of superconducting lead cavities as a function of time during a period of a month showed an oscillating variation. An explanation of the ageing curves is proposed.

The origin of the residual surface resistance of a superconducting surface has earlier been investigated experimentally by measurements of the dependence of the residual losses in superconducting lead and niobium cavities on frequency,[1-3] the mode in the cavity,[2-4] the

applied magnetic field,[1,5-7] and the treatment of the surface.[2,4,7-10] Some authors have observed a change of the residual surface resistance with time.[2,9] Long time measurements on niobium cavities have been reported.[11] In the present work, long time measurements on lead