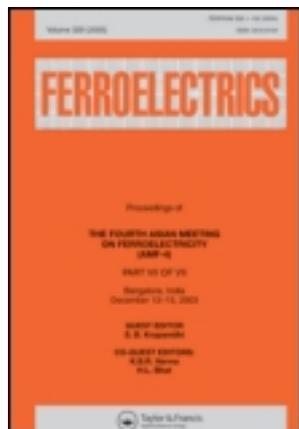


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INVESTIGATION OF THE RELATIONSHIP BETWEEN THE SPONTANEOUS POLARIZATION AND PERMITTIVITY IN TGS AND DTGFB

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The relationship, $p/\chi = P_s/C$, between the pyroelectric coefficient, p , dielectric susceptibility, χ , spontaneous polarization, P_s , and the Curie constant, C , has been experimentally tested in TGS and DTGFB by simultaneously measuring p , χ , and P_s . Good agreement was found for temperatures within approximately 20°C below the Curie point. The difference between p/χ and P_s/C at lower temperatures indicates that the Devonshire expansion of the free energy with temperature independent coefficients of high order terms, regardless of the number of terms included, cannot describe the ferroelectric behavior of TGS and DTGFB far below their transition temperatures.

INTRODUCTION

The thermodynamic model of Devonshire¹ has been successfully used to describe the ferroelectric behavior of TGS near its transition temperature T_c .²⁻⁴ According to this model, the thermodynamic potential, F , of a stress-free crystal can be expanded in powers of the electrical polarization P :

$$F(P, T) = F_0(T) + \frac{\beta(T - T_c)P^2}{2} + \frac{\gamma P^4}{4} + \frac{\delta P^6}{6} + \dots, \quad (1)$$

where the coefficients β , γ , δ , ... are usually assumed to be temperature independent. From this expansion, the isothermal dielectric susceptibility, χ , and the spontaneous polarization, P_s , can be derived using the thermodynamic relationships: $\chi = (\partial^2 F / \partial P^2)^{-1}$, and $(\partial F / \partial P) = 0$ at $P = P_s$. To describe the behavior of P_s and χ near the phase transition, it has been found sufficient to include in the expansion of F (Eq. 1) only the first four terms.^{2,3} Zerem and Halperin⁵ have attempted to extend the applicability of Devonshire's model to temperatures far below T_c by including an addition-

al term in the thermodynamic potential expansion. They included the eighth order term and found good agreement between experimental and calculated values of P_s in TGS from T_c down to about 100K. However, the results of the inclusion of the additional term to the calculation of other physical parameters, like the dielectric susceptibility were not presented.

In the present work we have experimentally studied a relationship derived from the Devonshire model and independent of the number of terms included in the thermodynamic potential expansion. This relationship was reported by Liu and Zook⁶ and is given by

$$\frac{p}{\chi} = \frac{P_s}{C}, \quad (2)$$

where $p = -\partial P_s / \partial T$ is the pyroelectric coefficient and $C = 1/\beta$ is the Curie constant. In the derivation of Eq. 2 it is assumed that the coefficients γ , δ , etc. in Eq. 1 are temperature independent. In the general case, this relationship takes the form:

$$\frac{p}{\chi} = \frac{\partial^2 F}{\partial T \partial P} = \frac{P_s}{C} + \left[\left(\frac{d\gamma}{dT} \right) P_s^3 + \left(\frac{d\delta}{dT} \right) P_s^5 + \dots \right]. \quad (3)$$

The ratio p/χ plays an important role in the characterization of ferroelectric materials as pyroelectric detectors, and its behavior has been

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studied in several materials.⁷⁻⁹ For the temperature dependence of p/χ in TGS, earlier investigators have obtained different results,⁷⁻⁹ and found no agreement with the calculated behavior of p/χ based on Devonshire's model, except in the immediate vicinity of T_c .^{7,9} This study was motivated by a desire to resolve the ambiguity in the literature with respect to the experimental behavior of p/χ in TGS. Measurement of all the parameters involved in Eq. 2 enabled us, in addition, to re-examine the prediction of the Devonshire model without the introduction of any adjustable parameters.

EXPERIMENTAL TECHNIQUE

The pyroelectric coefficient, p , and the dielectric susceptibility, χ , were measured simultaneously by a computer controlled system.¹⁰ The simultaneous measurement eliminates the error that would be introduced from temperature uncertainties in separate measurements of these parameters. The spontaneous polarization was determined by integrating the pyroelectric current, and the Curie constant was derived from the dielectric behavior

above the transition temperature using the Curie-Weiss law.

A block diagram of the measuring circuit is shown in Figure 1. The circuit was divided into high frequency and dc parts, electrically isolated at their respective frequencies. The dc half of the circuit was used for poling the crystal and measuring the pyroelectric current. The dielectric susceptibility was measured at 1 kHz through the high frequency half of the circuit with an 8 V/cm ac field. Automated control was accomplished with a Hewlett Packard 3052A Data Acquisition System. This system permitted up to 100 separate measurements of each of the four variables (χ , pyroelectric current, temperature and time) per degree.

Measurements were performed on samples of TGS obtained from the Quartz and Selice Company and samples of deuterated triglycine fluoroberyllate (DTGFB) grown at Philips Labs.¹¹ The samples were fully electroded with evaporated gold and were poled with a field of 4 kV/cm during cooling from above the Curie temperature to 0°C. Data were taken during the subsequent heating cycle through the Curie temperature at 2°C/min. under short circuit conditions.

EXPERIMENTAL RESULTS AND DISCUSSION

In Figures 2 and 3, the measured values of p/χ (circles) are plotted together with the measured values of P_s/C (solid line) for TGS and DTGFB. The adiabatic correction¹² was applied to obtain the isothermal values of χ used in the plots and

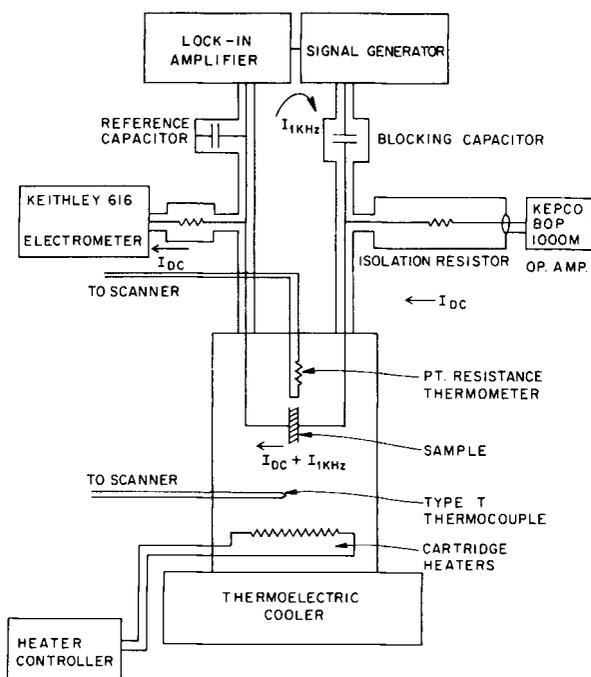


FIGURE 1 A block diagram of the circuit used for simultaneous measurement of the pyroelectric coefficient and dielectric constant.

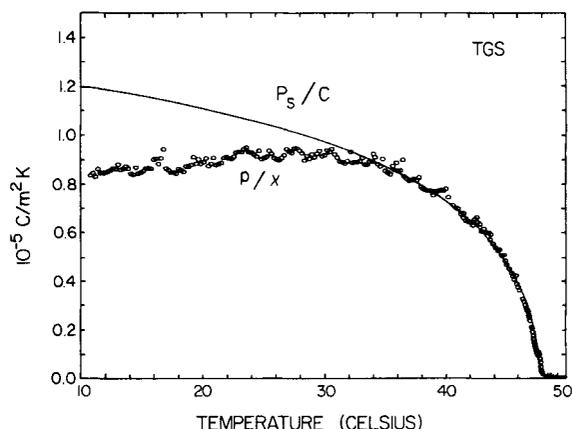


FIGURE 2 Experimental values of p/χ (circles) and P_s/C (solid line) for TGS.

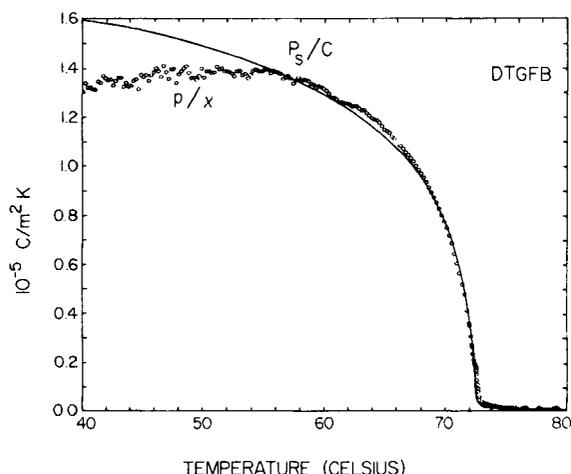


FIGURE 3 Experimental values of p/χ (circles) and P_s/C (solid line) for DTGFB.

Eq. 2. It is seen that for both materials good agreement exists between p/χ and P_s/C , as predicted by Eq. 2, from T_c down to approximately 20°C below the Curie temperature. However, as the temperature is lowered beyond that region, the values of p/χ increasingly deviate from the values of P_s/C .

The origin of these differences is not due to use of a limited number of terms in the thermodynamic potential expansion (Eq. 1), since Eq. 2 is valid for infinite terms in the expansion. However, the discrepancy may be due to neglecting the temperature dependence of the coefficients γ , δ , etc. According to Eq. 3, the effect of the temperature dependence of these coefficients becomes more important at low temperatures where P_s is large.

In conclusion, the ratio p/χ in TGS and DTGFB follows the prediction of Devonshire's model over

a significant range of temperatures (within 20°C of the Curie point). It may be possible to extend this agreement over a larger temperature range by introducing temperature dependence to the coefficients of higher order terms. Nevertheless, it is clear that the expansion of the thermodynamic potential without including temperature dependence of the coefficients of higher order terms, cannot properly describe the behavior of TGS and DTGFB far below their transition points. This conclusion is independent of the number of terms included in the thermodynamic potential expansion.

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