parameter b_6 is determined by the value of K_2 and has not been measured for EuO. The parameter b_6 is negative for both EuS and EuSe with the latter having the larger magnitude. At present this dependence of b_4 and b_6 on lattice spacing is not understood.

Experiments to determine K_1/M and K_2/M in EuO as well as the temperature dependence of the anisotropy constants in the three ferromagnetic europium chalcogenides are in progress. The results of these experiments, and in particular the temperature dependence, should more critically test the single-ion mechanism as being the source of magnetic anisotropy in this series of compounds.

SUMMARY

The first- and second-order magnetocrystalline anisotropy constants of EuSe are $K_1/M = -50\pm6$ Oe and $K_2/M = -83\pm16$ Oe. On the basis of Wolf's single-ion mechanism, the cubic crystal-field splitting parameters have been calculated to be $b_4 = (4.5\pm0.5)\times10^{-4}$ cm^{-1}/ion and $b_6 = -(1.3\pm0.3)\times10^{-4}$ cm^{-1}/ion. The comparison of these values with b_4 and b_6 determined from anisotropy measurements in EuO and EuS indicate a minimum in b_4 as a function of lattice spacing. This is in contrast to the monotonically increasing values of b_4 for Eu^{++} ions as a function of lattice spacing in oxide (CaO, SrO, and BaO) and fluoride (CaF, SrF, and BaF) host systems. The value of b_6 is negative and decreases with increasing lattice parameter for EuS and EuSe, which is consistent with the other cubic host systems.

ACKNOWLEDGMENTS

We thank H. W. White for furnishing the impurity analyses of the europium selenide used in the experiment. We also thank Dr. M. C. Franzblau for developing the computer program used to fit the resonant condition to the data.

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Dielectric, Thermal, and Pyroelectric Properties of Ferroelectric LiTaO$_3$

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Measurements of the dielectric constant κ, specific heat c_p, and pyroelectric coefficient dP_s/dT of LiTaO$_3$ have been made over the temperature range from 25 to 700°C. The experimental technique enabled all these measurements to be made simultaneously or consecutively on the same sample. In each of these measurements pronounced anomalies were observed at the ferroelectric Curie temperature $T_C = 618$°C, clearly indicating a transition of the second order. From the pyroelectric and specific-heat measurements, the temperature dependence of the spontaneous polarization has been obtained to within 5% accuracy. At temperatures T where $T/T_C \gtrsim 0.9$ it was found that $P_s^2 \propto (T-T_C)$ and $1/\kappa \propto (T-T_C)$, in accordance with thermodynamic theory, and the specific-heat data are entirely consistent with these measurements.

I. INTRODUCTION

It has been known for several years that LiTaO$_3$ is ferroelectric up to about 600°C.[1] Ferroelectric hysteresis loops were observed in this material under certain conditions, and the spontaneous polarization was found to be an increasing function of temperature up to 470°C.

Recently, a great deal of interest in this material has been revived owing to its large electro-optic coefficients and its use for devices.[2] However, with Czochralski-grown crystals[3] no ferroelectric hysteresis loops have been observed owing to the high coercive field at low temperatures, and the high conductivity at elevated temperatures. In this work attempts to switch LiTaO$_3$ below 500°C, using platinum electrodes, were unsuccessful. Even at 550°C the switching time was several minutes with 10 000 V/cm.

Two measurements of the spontaneous polarization P_s of LiTaO$_3$ have recently been reported. The first measurements, by a static pyroelectric technique,[4] yielded a room-temperature value of $P_s = 50\pm2\ \mu$C/cm^2. Measurements of P_s up to 450°C were reported in this work. The second measurements[5] were obtained by switching LiTaO$_3$ at room temperature using liquid electrodes and very high pulsed fields ($\sim5\times10^5$ V/cm). These experiments were limited to the temperature range 0 to 100°C since an aqueous electrolyte was used.

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[1] B. T. Matthias and J. P. Remeika, Phys. Rev. **76**, 1886 (1949).

[2] R. T. Denton, F. S. Chen, and A. A. Ballman, J. Appl. Phys. **38**, 1611 (1967).

[3] A. A. Ballman, J. Am. Ceram. Soc. **48**, 112 (1965).

[4] H. Iwasaki, N. Ushida, and T. Yamada, Japan. J. Appl. Phys. **6**, 1336 (1967).

[5] S. H. Wemple, M. DiDomenico, and I. Camlibel, Appl. Phys. Letters **12**, 209 (1968).

The value of P_s at room temperature was reported to be 50 ± 1 $\mu C/cm^2$, in excellent agreement with the first work. The reason for the dependence of switching on the nature of the electrodes is not clear, though it seems that the magnitude of the coercive field is associated with the behavior of the surface layers during switching.

The purpose of this work was to make accurate measurements of the dielectric and thermal properties of this important material over the temperature range from 25 to 750°C, in order that a detailed comparison with theory of the temperature dependence of these properties could be made. For this purpose the temperature range from 500 to 700°C is particularly important.

$LiTaO_3$ is isomorphous with $LiNbO_3$.[6] It is known to be a displacement ferroelectric with space group $R3c$ below the Curie temperature T_C, and becomes centrosymmetric (probably $R\bar{3}c$ [6,7]) above T_C.

It has been shown that there is a marked dependence of the properties of many ferroelectrics on the stoichiometry of the melt from which a crystal is grown.[8] In the case of $LiTaO_3$ the Curie temperature may change from 540 to 700°C depending on the growth conditions. The Curie temperature changes even along the length of a single crystal. For meaningful measurements of the ferroelectric properties of $LiTaO_3$ all measurements have to be made on the same specimen, which is small compared with the size of the parent crystal. This is accomplished by the procedures used in these experiments.

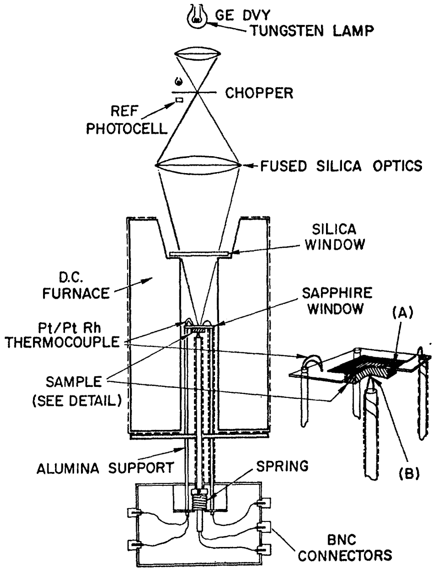

FIG. 1. Diagram of experimental apparatus.

To measure the temperature variation of the specific heat, the technique used is essentially that used by Handler *et al.*[9] to investigate the ferromagnetic phase transition of nickel. In this technique the crystal is pulse heated by a light beam and the temperature variation of the crystal is measured with a thermocouple. The measurement is proportional to the inverse specific heat of the crystal. This method requires only minute specimens, has a temperature resolution of about 1/200 °C, and is continuously recording as a function of temperature, so that it is especially useful in the investigation of phase transitions.

Measurements of the pyroelectric coefficient were made using the dynamic technique first used by Chynoweth.[10] The sample is again pulse heated with a light beam, resulting in a pyroelectric signal of amplitude

$$i=A\left(\frac{dP_s}{dT}\right)\frac{dT}{dt}=\left(\frac{dP_s}{dT}\right)\times\frac{W}{l\rho Jc_p},\qquad(1)$$

where A is the electroded area of the crystal, J the mechanical equivalent of heat, l the crystal thickness, ρ the density, and c_p the specific heat. The rate of heating (dT/dt) is constant during a light pulse, so changes in i reflect changes in the pyroelectric coefficient (dP_s/dT). It has been shown[4] that the difference between the pyroelectric coefficient measured at constant stress and that measured at constant strain is small for $LiTaO_3$ so the temperature dependence of the spontaneous polarization may be obtained by direct integration of the (dP_s/dT) curve.

The dielectric constant was measured in a straightforward way by means of a capacitance bridge.

In this work the experimental data are interpreted in terms of the thermodynamic theory of ferroelectrics,[11] in which the elastic Gibbs function is expanded in terms of even powers of polarization P:

$$\Delta G=\tfrac{1}{2}\beta(T-T_0)P^2+\tfrac{1}{4}\gamma P^4+\tfrac{1}{6}\delta P^6+\cdots.\qquad(2)$$

The temperature factor in the coefficient of P^2 is introduced[11] to account for the observed linear temperature dependence of the reciprocal dielectric susceptibility above the Curie temperature where $P\simeq0$. The polarization, dielectric susceptibility χ, and entropy change ΔS may be obtained from this expression by means of the well-known thermodynamic relations

$$E=(\partial G/\partial P)_T=0\qquad\text{for zero applied electric field,}$$

$$\chi^{-1}=(\partial^2G/\partial P^2)_T=4\pi/\kappa\qquad\text{for dielectric constant }\kappa\gg1,$$

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[6] S. C. Abrahams and J. L. Bernstein, J. Phys. Chem. Solids **28**, 1685 (1967); S. C. Abrahams, W. C. Hamilton, and A. Sequeira, *ibid.* **28**, 1693 (1967).

[7] A. S. Barker, Jr., and R. Loudon, Phys. Rev **158**, 433 (1967).

[8] A. A. Ballman, H. J. Levinstein, C. D. Capio, and H. Brown, J. Am. Ceram. Soc. **50**, 657 (1967); A. A. Ballman and H. Brown, J. Crystal Growth **1**, 311 (1967); J. C. Bergman, A. Ashkin, A. A. Ballman, J. M. Dziedzic, H. J. Levinstein, and R. G. Smith, Appl. Phys. Letters **12**, 92 (1968).

[9] P. Handler, D. E. Mapother, and M. Rayle, Phys. Rev. Letters **19**, 356 (1967).

[10] A. G. Chynoweth, J. Appl. Phys. **27**, 78 (1956).

[11] A. F. Devonshire, Advan. Phys. **3**, 85 (1954), and references quoted therein.

and

$$\Delta S = S - S_0 = -(\partial G/\partial T)_P.$$

$$(S_0 = \text{entropy at } T_C = 618°\text{C.})$$

Thus the change of specific heat is given by

$$\Delta c_p = T(dS/dT).$$

Above the Curie temperature T_C, where $P \simeq 0$, we have

$$4\pi/\kappa = \beta(T - T_0). \qquad (3)$$

If we make only the assumption that the coefficients β, γ, and δ are independent of temperature, then

$$\Delta S = -\tfrac{1}{2}\beta\Delta P^2 \quad \text{and} \quad \Delta c_p = -\tfrac{1}{2}\beta T(\partial P_s^2/\partial T). \qquad (4)$$

If we make the additional assumption that terms higher than P^6 in the expansion of ΔG may be neglected, then considering the case of a second-order transition,[12]

$$P_s^2 = (\gamma/2\delta)[(1 - 4\delta\beta\gamma^{-2}(T - T_0))^{1/2} - 1] \qquad (5)$$

and

$$\kappa^{-1} = (\beta(T - T_0) + 3\gamma P^2 + 5\delta P^4)/4\pi. \qquad (6)$$

If the term in P^6 is neglected, these equations reduce to the familiar relations

$$P_s^2 = -(\beta/\gamma)(T - T_0) \qquad (7)$$

and

$$\kappa^{-1} = -(\beta/2\pi)(T - T_0). \qquad (8)$$

The above approximations are examined in Sec. IV in an attempt to describe all the experimental data in terms of this theory.

Part of the stimulus for this work is the advent of a statistical theory of ferroelectrics for which a complete set of data was required. Interpretation of the data of this report in terms of this new theory will appear in a future publication.[13]

II. EXPERIMENTAL PROCEDURE

Large single crystals of $LiTaO_3$ were pulled from a stoichiometric melt by Ballman.[3] The crystals were poled, and specimens were cut and mechanically polished into wafers of dimensions $\sim 0.3 \times 0.3 \times < 0.01$ cm^3 with the crystallographic c axis normal to the plane of the wafers. The two faces of the wafers were electroded with platinum paste and fired at temperatures less than 600°C.

The wafers were lightly clamped in the apparatus shown in Fig. 1. Pressure contact to the lower electroded face was made with a Chromel-Alumel thermocouple junction B and to the upper face with platinum foil A. A hole in the foil A allowed chopped light from the high-temperature tungsten lamp (G.E.DVY) to fall on the face of the wafer, and also masked the edges of the wafer from the light.

The specimen holder was mounted inside a dc-powered platinum furnace which was heated at about 5°C/min while the capacitance, specific heat, and/or pyroelectric current were measured as functions of temperature.

Capacitance Measurements

The dielectric constant of the wafers was measured at 1 kHz on a General Radio (type 1673-A) capacitance bridge which compensates for sample conductance. The output of the bridge was recorded on the Y axis of an X-Y recorder, while the specimen temperature was recorded on the X axis by means of a Pt/PtRh thermocouple placed next to the crystal.

Specific-Heat Measurements

Light from the tungsten lamp was mechanically chopped at 30 cps with a 50% duty cycle. The temperature change of the crystal during the pulse heating by the light beam was detected with the thermocouple B connected to a lock-in amplifier (P.A.R. model HR8). The output of the amplifier was recorded as a function of temperature on an X-Y recorder. The circuit is shown schematically in Fig. 2.

The output signal of the lock-in amplifier E is proportional to the temperature change of the specimen (in terms of the thermocouple response $d\varphi/dT$) when energy W is absorbed by the crystal.

Thus

$$E \propto (d\varphi/dT)(W/c_p). \qquad (9)$$

The thermal capacity of the thermocouple junction was less than 0.01% of that of the irradiated volume of the crystal, so it has been neglected. The thermal diffusion time constant of the specimen was estimated to be less than 10^{-3} sec so that the output signal was not a function of the thermal diffusivity of the crystal. (In practice this was validated since the results were independent of specimen thickness below 0.01 cm.)

Now $d\varphi/dT$ is a slowly varying function of temperature T, and it is also possible that W is a function of T because of changes in electrode reflectance and window transmission over the large temperature range. So to

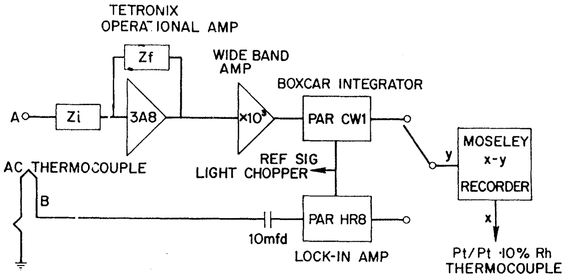

FIG. 2. Schematic of detection electronics for specific-heat and pyroelectric measurements.

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[12] E. Fatuzzo and J. W. Merz, *Selected Topics in Solid-State Physics*, edited by E. P. Wohlfarth (John Wiley & Sons, Inc., New York, 1967), Vol. VII.

[13] M. E. Lines (to be published).

transform the recorded curve to a curve of c_p^{-1} versus T, the identical experiment was performed using a platinum specimen, 0.0075 cm thick, having fired platinum paste electrodes. Then

$$\frac{E(\mathrm{LiTaO_3})}{E(\mathrm{Pt})} \propto \frac{c_p(\mathrm{Pt})}{c_p(\mathrm{LiTaO_3})}.$$

c_p is known as a function of temperature to a high degree of accuracy,[14] so the temperature variation of $c_p(\mathrm{LiTaO_3})$ could be obtained (in arbitrary units) with an accuracy of about 0.5% over a 100°C interval, with a resolution of about 1/200°C.

The platinum electrodes were opaque to the incident radiation, so no correction need be made for temperature variations of the crystal absorbance. The specimen was heated by conduction from the upper electrode.

The above technique yields the variation of specific heat with temperature. To obtain absolute values of c_p a point on the curve has to be calibrated. This was done by calibrating LiTaO$_3$ against LiNbO$_3$ (for which c_p is known[15]) using a simple dropping technique with a copper calorimeter, to an accuracy of about 10%.

Pyroelectric Measurements

As for specific-heat measurements, the samples were pulsed heated with the light beam at 30 cps. Electrode A was connected to an operational amplifier with input impedance $Z_i=0$ and feedback impedance $Z_f=100$ kΩ (see Fig. 2). The effective input impedance to the signal was thus Z_f/A, where A is the open loop amplifier gain (~15 000). In this way no voltage developed across the crystal during a heating pulse, so no correction need be made for sample conductance. This is important for crystals like LiTaO$_3$, which become fairly conducting at elevated temperatures. The voltage signal iZ_f was amplified and fed into a boxcar integrator (P.A.R. model CW1) and the output was recorded as a function of temperature on an X-Y recorder.

Pyroelectric measurements were also made with light chopped at 120 cps and a 10% duty cycle. The peak pyroelectric current was the same at all temperatures as with the previous chopper, indicating that there was no significant heating of the sample by the light beam. The advantage of the boxcar integrator is that the shape of the pyroelectric signals can be examined, even when they are below the noise level, as well as being a phase-sensitive detector for low duty cycle signals. In all cases the signals were square waves as expected.[10] (For low-conductance crystals this circuit may be used for measurement of sample capacitance, by using capacitative Z_f and the sample as capacitor Z_i. The amplifier gain is then Z_f/Z_i.)

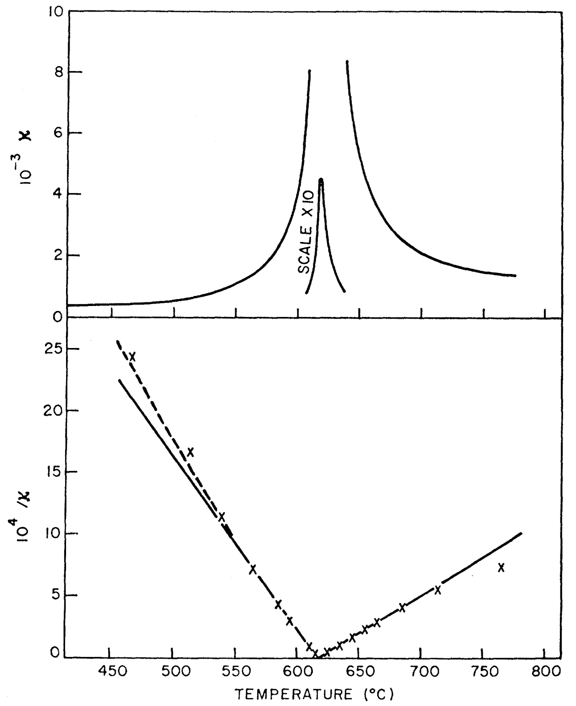

FIG. 3. Temperature variation of dielectric constant κ and κ^{-1} for LiTaO$_3$.

III. RESULTS

Capacitance Measurements

The temperature variation of the dielectric constant of LiTaO$_3$ along the c axis in the range 400 to 800°C is shown in Fig. 3. A pronounced anomaly is seen at the ferroelectric Curie temperature $T_C=618$°C with a peak value ϵ about three orders of magnitude greater than the room-temperature value. In Fig. 3 a plot of $1/\kappa$ shows that for $|T-T_C|<100$°C a Curie-Weiss law is obeyed, with a Curie-Weiss temperature T_0 equal to the Curie temperature T_C. The gradient of the graph for $T>T_C$ yields a Curie constant

$$C=(1.6\pm0.05)\times10^5\ {}^\circ\mathrm{C},$$

a value which is typical of this type of displacement ferroelectric. For $T<T_C$ the gradient of the $1/\kappa$ versus T graph is

$$-1/(0.72\pm0.03)\times10^5\ {}^\circ\mathrm{C}^{-1}.$$

The main error in the measurement of κ between 400 and 800°C is the 2% error in the measurement of the electroded area of the crystal. The error in T (and hence T_C) is less than 2%.

Specific-Heat Measurements

The corrected curve of c_p versus T for LiTaO$_3$ is shown in Fig. 4. A discontinuity in the specific heat is observed at the ferroelectric Curie temperature $T_C=618$°C, but there is no latent heat associated with the transition.

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[14] F. M. Jaeger and E. Rosenbaum, Physica **10**, 1123 (1939).

[15] L. B. Pankratz and E. G. King, Bur. Mines. Report No. 6862, 1966 (unpublished).

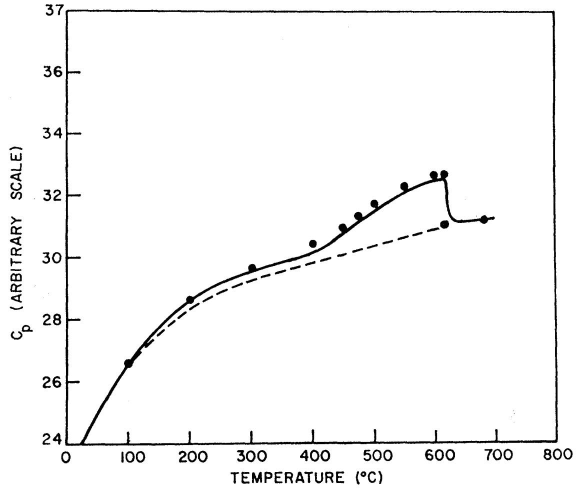

FIG. 4. Temperature variation of the specific heat c_p of $LiTaO_3$. Solid curve, experiment corrected for thermocouple response and W (see text). Dashed curve, background specific heat. ●, c_p calculated from the data of Figs. 3 and 6.

The calibration of $LiTaO_3$ against $LiNbO_3$ by the dropping technique gave

$$c_p(\mathrm{LiTaO_3}) = (1.1\pm0.1)\times c_p(\mathrm{LiNbO_3})$$

from 25 to 150°C. Using the published data for $LiNbO_3$[15] we obtain $c_p(\mathrm{LiTaO_3}) = 24\pm2$ cal mole^{-1} °C^{-1} at 25°C, so the ordinate in Fig. 4 is c_p in units of cal mole^{-1} °C^{-1}.

The large variation of c_p with temperature between 25 and 700°C is consistent with the high value of the Debye temperature[16] of this material.

The heat ΔQ and entropy ΔS associated with the ferroelectric transition is difficult to obtain with any accuracy since the "background" specific-heat curve is not known. A minimum value may be obtained by taking the excess specific heat as zero at 400°C. Then

$$\Delta Q = \int_{400^\circ\mathrm{C}}^{T_C} c_p dT = 210 \text{ cal/mole}$$

and

$$\Delta S = \int_{400}^{T_C} (c_p/T) dT = 0.23 \text{ cal/mole °C}.$$

These quantities and the significance of the broken line in Fig. 4 will be discussed further in Sec. IV.

Pyroelectric Measurements

The pyroelectric current i is plotted as a function of temperature in Fig. 5. Once again a pronounced discontinuity is observed at $T_C = 618$°C. Above this temperature the pyroelectric current decreased rapidly to zero and there was no evidence of any space charge effects.[17] The results were unaltered when crystals were repoled after specimen preparation indicating that no depoling of the crystals took place during specimen preparation. The curves were reproducible using crystals etched in HNO_3+HF before electroding.

Equation (1) shows that the pyroelectric current i is a function of c_p and W as well as dP_s/dT. Now W/c_p can be obtained from the measurements of the Sec. II [see Eq. (9)]. Thus

$$i = \frac{E(dP_s/dT)}{l\rho J\,(d\varphi/dT)}\,.$$

$d\varphi/dT$ was obtained from the calibration of φ versus T. The broken line in Fig. 5 is the i versus T curve corrected for the temperature variation of W/c_p. This curve is accurate to within 5%.

For a second-order ferroelectric-paraelectric transition the spontaneous polarization may be obtained in arbitrary units by direct integration of the dP_s/dT versus T curve, i.e.,

$$P_s^T = \int_{T_C}^{T} (dP_s/dT) dT.$$

This curve is shown in Fig. 6 with the data normalized

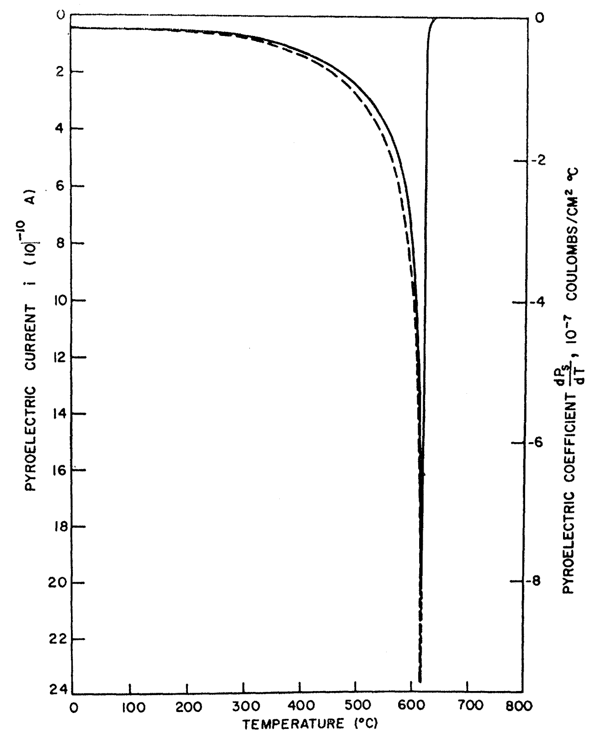

FIG. 5. Temperature variation of pyroelectric current i and pyroelectric coefficient dP_s/dT of $LiTaO_3$. Solid curve, experiment; dashed curve, corrected for temperature variation of c_p and W.

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[16] From measurements of c_p at low temperature $\Theta_D = 449$°K [J. Marta (private communication)]. Calculated from measurements of elastic constant $\Theta_D = 535$°K at 25°C [J. Bergman (private communication)]. From x-ray diffraction measurements $\Theta_D = 452$°K at 25°C (Ref. 6).

[17] A. G. Chynoweth, Phys. Rev. **102**, 705 (1956); **117**, 1235 (1960)

so that $P_s^0=1$ at 0°K. (The pyroelectric data were extrapolated to 0°K with a resulting error in P_s^0 of less than 2%.) Over the temperature range $T_C-T<120$°C, $(P_s)^2$ is seen (Fig. 6) to be a linear function of T

$$(P_s)^2=2.88\times T\times (P_s^0)^2\times 10^{-3}.$$

The spontaneous polarization curve must be calibrated at one point in order to obtain an absolute curve of P_s versus T. Two workers[4,5] have arrived at the same value of $P_s^{300}=50\pm2$ μC/cm² by different techniques. It is unlikely that variations of crystal stoichiometry will alter the value of P_s^{300} by more than 2%. This calibration yields the value $P_s^0=53\pm4$ μC/cm², and a value for the room-temperature pyroelectric coefficient of $LiTaO_3$ of 0.019±0.001 μC cm^{-2} °C^{-1}. This value may be the most accurate value of dP_s/dT published for any material, and could serve as a calibration for other pyroelectric investigations.

Out of interest, the pyroelectric coefficient of $LiTaO_3$ at 27°C was calibrated against that of $BaTiO_3$ measured under identical conditions. It was found that

$$(dP_s/dT)_{\mathrm{LiTaO_3}}{}^{300}=(0.8\pm0.1)\,(dP_s/dT)_{\mathrm{BaTiO_3}}{}^{300},$$

using for $BaTiO_3$: $\rho=6.0$ g/cc, $c_p=28$ cal/mole °C, and for $LiTaO_3$: $\rho=7.45$ g/cc,[18] $c_p=24$ cal/mole °C. In Ref. 10 an approximate value of (dP_s/dT) for $BaTiO_3$ at room temperatures is given as 2×10^{-2} μC/cm² °C, which gives $(dP_s/dT)_{\mathrm{LiTaO_3}}{}^{300}=(0.016\pm0.002)$ μC/cm² °C in fair agreement with the above value. This method is, however, less accurate than the direct methods[4,5] of measuring P_s since the calibration is very sensitive to slight variations in the conditions of measurement from one sample to another, and dP_s/dT for $BaTiO_3$ has not been accurately reported.

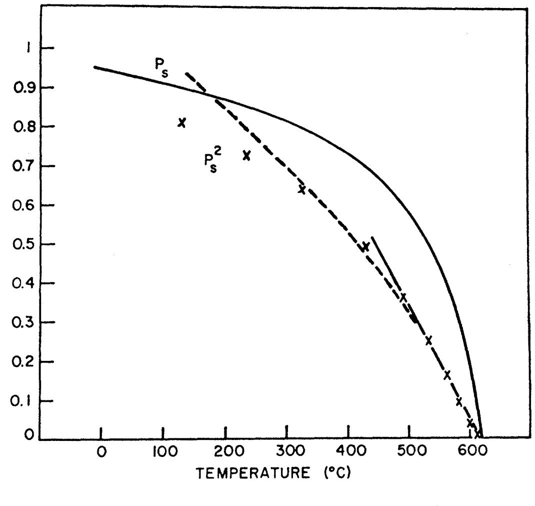

FIG. 6. Solid curve, temperature variation of spontaneous polarization P_s obtained by integration of Fig. 5. ×, corresponding values of P_s^2 versus T. Dashed curve and dashed curve with ×'s, calculated curves of P_s^2 versus T. The abscissa is normalized so that P_s and $P_s^2=1$ at 0°K.

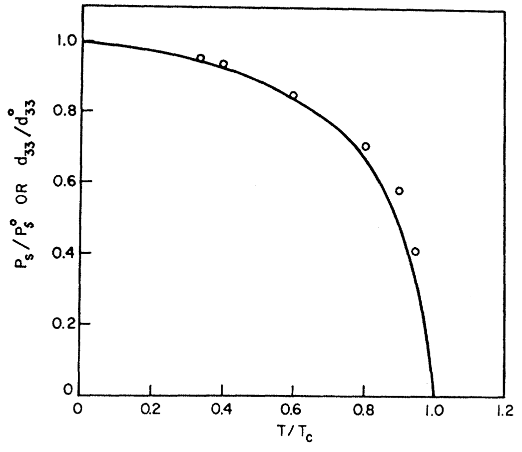

FIG. 7. Comparison of the temperature variation of spontaneous polarization P_s with that of the nonlinear coefficient d_{33} from second harmonic generation experiments (see Ref. 21). The ratios P_s/P_s^0 (solid curve), and d_{33}/d_{33}^0 (open circles) are given for convenience.

Errors: Reproducibility of all the foregoing results from one specimen was better than the errors quoted, since it was estimated that random errors were smaller than systematic errors. The latter were to some extent compensated for by the calibration procedures used, but their magnitude is not known accurately. Therefore, the errors quoted are the estimated maximum errors.

IV. DISCUSSION

In contradiction to early work[1] on flux-grown material, the spontaneous polarization of $LiTaO_3$ was found to be a decreasing function of temperature. The shape of the polarization curve up to 450°C was found to be in excellent agreement with the recent work of Iwasaki *et al.*[4]

The absence of any latent heat of transition proves unambiguously that the ferroelectric-paraelectric phase transition of $LiTaO_3$ at 618°C is a second-order transition. Observations of the high peak value of the dielectric constant, that $T_0=T_C$, of the large temperature range over which Δc_p is significant, and that there is no discontinuity in the thermal expansion of $LiTaO_3$ at the Curie temperature[19] are all consistent with this result.

In this section an attempt is made to account for the experimental results of Sec. III in terms of the thermodynamic theory of ferroelectrics.

At temperatures near T_C where $|\epsilon|<0.1$ $[\epsilon\equiv(T-T_C)/T_C]$, the well-known linear relationships $P_s^2\propto(T-T_C)$ and $1/\kappa\propto(T-T_C)$ are experimentally verified for $LiTaO_3$. In thermodynamic theory, these relationships are only valid when the coefficients β and

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[18] R. L. Barnes (private communication).

[19] C. D. Capio (private communication).

TABLE I. Value of the heat ΔQ and entropy ΔS of order of LiTaO$_3$, evaluated between temperatures T and T_C.

T(°K)	Experimental $[\Delta Q]_{T_C}{}^T$	 $[\Delta S]_{T_C}{}^T$	Semiempirical $[\Delta Q]_{T_C}{}^T$	 $[\Delta S]_{T_C}{}^T$	Theoretical $[\Delta Q]_{T_C}{}^T$	 $[\Delta S]_{T_C}{}^T$
773	179	−0.20	210	−0.253	211	−0.253
673	252	−0.30	314	−0.406	318	−0.404
573	284	−0.353	368	−0.498	397	−0.531
473	311	−0.416	396	−0.565	456	−0.645
300	334	−0.514	430	−0.663	493	−0.811
0			440	−0.751	509	−1.025

γ in the expansion of the elastic Gibbs function [Eq. (2)] are assumed to be temperature-independent, and only when terms higher than the fourth power in the expansion are negligible. The departure from linearity of the $P_s{}^2$ and κ^{-1} versus T curves when $|\epsilon|>0.1$ means that either higher powers in the expansion or the temperature dependence of the coefficients must be taken into account.

In the previous section it was found that the temperature dependence of the dielectric constant measured adiabatically is, for

$$-0.1>\epsilon>0, \qquad \kappa^{-1}=6.26\times10^{-6}\times(T-T_C) \qquad (10)$$

and for

$$-0.1<\epsilon<0, \qquad \kappa^{-1}=-1.39\times10^{-5}\times(T-T_C). \qquad (11)$$

The ratio of the two gradients is -2.23 ± 0.08. Correcting the dielectric constant to isothermal values,[12] this ratio becomes -2.11 ± 0.08. The theoretical value of this ratio, when terms higher than P^4 in Eq. (2) are neglected, is -2.0 in fair agreement with the experimental value, but outside the experimental errors. This suggests that even in the temperature range $|\epsilon|<0.1$ terms higher than P^4 may be of significance, or β and γ are functions of temperature.

From Eqs. (3) and (10) we have

$$\beta=7.86\times10^{-5}\ {}^\circ\mathrm{C}^{-1}.$$

Using the value of $P_s{}^0=53\ \mu\mathrm{C/cm}^2$, Eq. (7) can be fitted to the experimental data for $P_s{}^2$ versus T in the region $|\epsilon|<0.1$ with

$$\gamma=9.71\times10^6\ \mathrm{cm}^4/\mathrm{C}^2.$$

An attempt was made to obtain a better fit to the experimental data for $|\epsilon|>0.1$ by including the term in P^6 in the expansion of G [Eq. (2)], still assuming that β, γ, and δ are temperature-independent. A best fit of the data of Fig. 6 in the region $0>\epsilon>-0.3$ was computed by varying γ and δ, but leaving β at the above value since it is not significantly affected by the P^6 term. The best fit was obtained with

$$\gamma=8.04\times10^6 \quad \text{and} \quad \delta=2.42\times10^{15},$$

and is shown as a broken line in Fig. 6. It is seen that there is still a marked difference between the experimental and calculated curves where $\epsilon<-0.35$. This discrepancy could not be reduced with other values of γ and δ without diminishing the agreement at higher temperatures. However, it could be reduced by considering still higher terms in the expansion of G. It is likely that the effect of including more parameters is to compensate for the neglect of the temperature dependence of β, γ, and δ over the large temperature range.

Using these "best fit" values of γ and δ, the temperature variation of the reciprocal dielectric constant was computed from Eq. (4) for $T<T_C$. This is shown as a broken line in Fig. 3. The agreement with experiment is seen to be excellent for $0>\epsilon>-0.2$. Including the sixth power term has the effect of increasing the ratio

$$\frac{[\kappa(T-T_C)]_{T<T_C}}{[\kappa(T-T_C)]_{T>T_C}},$$

as observed experimentally, and it accounts for the observed departure from linearity of κ^{-1} versus T where $\epsilon<0.1$.

It is apparent from Eq. (4) that the temperature variation of the excess specific heat Δc_p due to the ferroelectric transition involves no new parameters, but can be directly calculated from the results of dielectric constant and spontaneous polarization measurements. Thus Δc_p was calculated using values of $\partial P_s{}^2/\partial T$ obtained graphically from Fig. 6, and the above value of β. Again $P_s{}^0=53\ \mu\mathrm{C/cm}^2$ was used. Comparison of the calculated values with the experimental curve is somewhat difficult since the "background" specific heat is unknown. It was evident from the calculations that there is significant contribution to Δc_p below 400°C. Thus the background curve was adjusted so that a fit to the experimental data was good where Δc_p was small—that is, above T_C and below about 100°C—and a smooth background curve was drawn through these points. This curve is shown as a broken line in Fig. 4. The values of Δc_p measured from this line are also shown. The agreement between the calculated and experimental shapes is excellent, but the calculated values are about 15% larger than the experimental ones. This difference may be due to errors in the values of c_p or $P_s{}^0$. (If $P_s{}^0$ is arbitrarily reduced to 49 μC/cm^2 the agreement with experiment is excellent.)

To compute the total heat $\Delta Q=(Q-Q_0)$ and entropy $\Delta S=S-S_0$ associated with the ferroelectric transition the integrals

$$[\Delta Q]_{T_C}{}^T=\int_{T_C}^{T}\Delta c_p dT$$

and

$$[\Delta S]_{T_C}{}^T=\int_{T_C}^{T}(\Delta c_p/T)dT$$

must be evaluated to $T=0$°K. However, c_p was only measured to 300°K. The value of ΔS is particularly sensitive to the choice of "background" specific heat at low temperatures. In Table I the integrals are evaluated for various values of T. The first two columns list $[\Delta Q]_{T_C}{}^T$ and $[\Delta S]_{T_C}{}^T$ obtained by direct integration of the experimental curves using the broken line of Fig. 5 as the baseline. The second two columns list these quantities evaluated from the experimental curve of $P_s{}^2$ versus T, while the last column lists these quantities evaluated with the "best fit" values of γ and δ given above. The agreement between the experimental and calculated values is of course limited to the agreement between the experimental and calculated values of Δc_p. At low temperatures the last column gives poor agreement with experiment as expected from the discussion above.

Finally, two interesting observations are worth noting.

(1) The experimental curve of P_s versus T and of the nonlinear coefficient d_{33} obtained from second harmonic generation experiments[20] are shown in Fig. 7. It is seen that to a good approximation

$$P_s{}^T \propto d_{33}{}^T.$$

This relationship has already been observed in $BaTiO_3$ [21] and has been predicted theoretically.[22]

(2) If the spontaneous polarization of $LiTaO_3$ is assumed to be entirely due to the ionic displacements from a centrosymmetric structure (i.e., no electronic polarization), and if the crystal is purely ionic (i.e., $Li^{+1}Ta^{+5}O_3{}^{-2}$), then P_s may be calculated from the relation

$$P_s=(e/V)\sum_i Z_i x_i,$$

where x_i is the displacement of an ion of charge Z_i from the position it occupies in the centrosymmetric (paraelectric) phase, e is the electronic charge, and V is the volume over which the summation is made. Using the structure data of Abrahams *et al.*[6] we find

$$P_s=(48\pm3)\ \mu\text{C/cm}^2 \qquad \text{at } 300°\text{K}.$$

The agreement with the measured value of $P_s=50$ μC/cm^2 at room temperature is remarkable when we consider the two assumptions made in this calculation. The nuclear-magnetic-resonance data of Peterson and Bridenbaugh[23] suggest that the charges on the oxygen and tantalum ions are smaller than the formal charges.[24] It is possible that the errors arising from these assumptions are mutually compensating.

V. CONCLUSION

The experimental technique enables the temperature dependence of the dielectric constant, specific heat, and spontaneous polarization of a ferroelectric to be obtained with sufficient accuracy for a detailed comparison with theory to be made. The ferroelectric-paraelectric phase transition of $LiTaO_3$ has been shown to be of the second order. In addition the dielectric and thermal properties of $LiTaO_3$ may be adequately accounted for by thermodynamic theory in the temperature range 300 to 700°C, using an elastic Gibbs function

$$\Delta G=7.86(T-T_C)P^2\times10^{-5}+8.04P^4\times10^6+2.42P^6\times10^{15}.$$

It is apparent that within the approximations of constant coefficients and neglect of terms higher than P^6 in the Gibbs function expansion thermodynamic theory cannot account for the experimental data over the whole temperature range.

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