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Primary and secondary contributions to spontaneous polarization of $LiNbO_3$ below 50 K

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The spontaneous polarization of $LiNbO_3$ has been measured in the $2.3 < T < 50$ K interval, by using a charge-integration technique. These data have been comparatively fitted for $T < 22$ K to a relation of the form $aT^n + bT^4 + ce^{-\Theta/T}$ with different n values. An estimation of the secondary pyroelectric coefficient favors the value $n = 2$. A comparison with $LiTaO_3$ has been made within the framework of the Born theory.

I. INTRODUCTION

Near to absolute zero the temperature variation of optical modes in ferroelectric materials is negligible. In these materials, which can be therefore considered at low temperature as conventional pyroelectrics, Lawless[1] has found an extra contribution to the heat capacity in addition to the Debye T^3 term. This contribution varies as $T^{3/2}$ for triglycine sulfate (TGS), potassium dihydrogen phosphate (KDP), $BaTiO_3$, and $LiNbO_3$. In this range there are several theories on the primary pyroelectric coefficient p_0, which gives the variation with temperature of the spontaneous polarization under constant strain, P_0. On the basis of acoustic-phonon contributions, Born[2] has proposed a theory predicting the behavior, $p_0 \propto T$, Born and Huang,[3] $p_0 \propto T^3$, Gonzalo,[4] $p_0 \propto T^{1/2}$, and Szigeti,[5] $p_0 \propto T^3$, all basing their theories on different arguments. Lang,[6] for lithium sulfate monohydrate and Lines,[7] for $LiTaO_3$, have interpreted their experimental data in terms of a T dependence according to Born theory. However, for ZnO (Ref. 8) and TGS,[9] T^3 and $T^{1/2}$ dependences have been experimentally found at low temperatures.

All these data show that the present understanding of these materials at low temperatures is very limited indeed. For the higher temperature range, when the polar optical modes are sufficiently excited, Lang[6] and Lines and Glass[10] have observed that p_0 is in agreement with the old theory of Boguslawski.[11]

In this paper we analyze the spontaneous polarization behavior of $LiNbO_3$, from 2.3 to 50 K. This is an interesting case for the following reasons.

(i) Due to the high Curie temperature (1400 K) of this compound, any softening of the optical modes may be neglected throughout the range of measurements.

(ii) Its high Debye temperature ($\Theta_D = 560$ K) allows a relatively large temperature range in which the behavior of the thermal expansion must be dominated by Debye-type contributions, which can be calculated with existing data. This is necessary in order to compute the contributions due to the crystal deformation.

(iii) This material is of technological importance in the field of radiation detection.

(iv) For the studied range of temperatures, the data may be compared to the results of Glass and Lines,[12] for $LiTaO_3$, this being isomorphous with $LiNbO_3$.

II. EXPERIMENTAL AND RESULTS

The sample was cut from a large single crystal 0.37 cm thick, with the base of 1.45-cm^2 surface perpendicular to the c axis. The crystal was grown by L. Arizmendi from congruent melt by the pulling method. After polishing, it was polarized, i.e., forced into a monodomain state in O_2 atmosphere to avoid reduction, by means of a field of 20 V/cm applied at a temperature of 1100 °C. The temperature was lowered at a rate of 20 °C/h and the field was suppressed at $T \simeq 800$ °C. Two sets of measurements were taken at low temperatures with the same sample within an interval of five months, the latter in order to obtain additional information on the behavior at the lower temperatures. For these measurements, the sample faces were polished once again. The reproducibility was excellent.

While this paper was under revision, new measurements in the temperature range $80 < T < 289$ K were made. The charge released by the single-domain sample was 0.90 μC/cm^2. A second experiment on a different sample, grown by the same method and of the same composition but not forced into single-domain state, yielded 0.70 μC/cm^2 in this temperature interval. Measurements on the interval $2.3 < T < 30$ K have been performed recently for the last sample. These results are in very good agreement with those reported in this paper, after being corrected for different areas and polarization states of

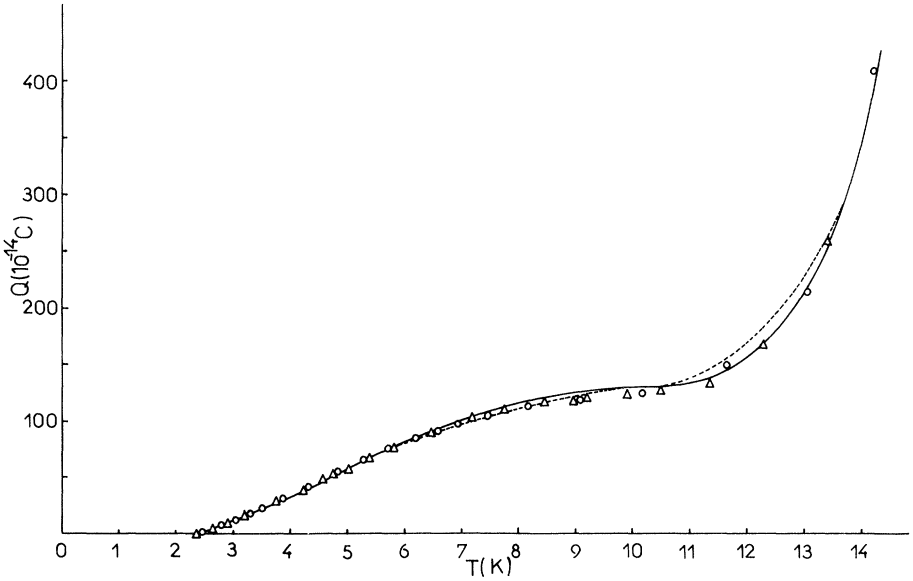

FIG. 1. Change of released charge with temperature between $2.3 < T < 14$ K. Circles and triangles correspond to two sets of measurements. The full curve corresponds to $n = 2$ fitting, while the dashed curve corresponds to $n = \frac{3}{2}$.

the samples. Details of my experimental setup and spontaneous polarization-measurement technique have been published elsewhere.[9,13]

The quantity I measure is the charge dQ released ($dQ > 0$) or gained ($dQ < 0$) by the sample surface area, A, perpendicular to the c axis, when the temperature is increased by dT. The equation $dP_s' = -(dQ/A)$, relates the change in spontaneous polarization dP_s' with the measured dQ, and the negative sign comes from the above criteria for the sign of dQ. The spontaneous polarization is written with a prime because this quantity is not the same as the electric dipole per unit volume P_s. Glass and Lines[12] have shown that the relation between the changes in these magnitudes, when the temperature changes dT, is for $LiNbO_3$

$$dP_s' = dP_s + 2\alpha_1 P_s dT \ ,$$

where α_1 is the linear thermal expansion coefficient in the direction perpendicular to the ferroelectric axis.

Following the arguments in Ref. 12, dP_s includes two terms, the primary pyroelectric polarization, dP_0, which takes place in the unstrained crystal, and the secondary, dP_1, which is strain induced via the piezoelectric effect. The latter reduces using symmetry restriction for crystals in class $3m$ to

$$dP_1 = 2e_{31}\alpha_1 dT + e_{33}\alpha_3 dT \ .$$

α_j are the linear thermal expansion coefficients in the direction j and e_{3j} the piezoelectric stress constants.

With the above equalities one obtains

$$dP_s' = -\frac{dQ}{A} = dP_0 + 2\alpha_1 P_s dT + 2e_{31}\alpha_1 dT + e_{33}\alpha_3 dT \ . \tag{1}$$

Integration between 0 and T yields

$$-\Delta P_s' = \frac{Q}{A} = -\Delta P_0 - \frac{1}{2}\left[a_1(P_s + e_{31}) + \frac{a_3}{2}e_{33}\right]T^4 \ , \tag{2}$$

where we suppose that the temperature is low enough relative to the Debye temperature Θ_D, to assume $\alpha_j = a_j T^3$.

Figure 1 shows the experimental data of Q vs T between 2.3 and 14 K and in Fig. 2, $\ln Q$ vs $1/T$ for $12 < T < 46$ K. These results were fitted using the expansion

$$Q(T) - Q(2.3) = aT^n + bT^4 + ce^{-\Theta/T} + d \ . \tag{3}$$

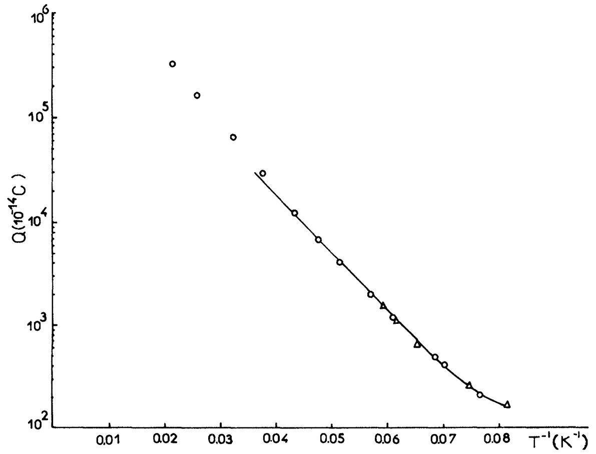

FIG. 2. Semilog plot of Q vs $1/T$ between $12 < T < 46$ K. The curve corresponds to $n = 2$ fitting.

TABLE I. Two schemes with four free parameters are presented for $n = 2$ and $n = \frac{3}{2}$. The temperature limit for both fits is $T = 22$ K. The third row represents a five-parameter fit, leaving the exponent n free, for $T < 14.5$ K. The errors which follow the coefficient values are the statistical errors of the fit.

n	$a\left(10^{-14}\frac{\text{C}}{\text{cm}^2\,\text{K}^n}\right)$	$b\left(10^{-16}\frac{\text{C}}{\text{cm}^2\,\text{K}^4}\right)$	$c\left(10^{-8}\frac{\text{C}}{\text{cm}^2}\right)$	Θ (K)
2	2.48 ± 0.02	-1.57 ± 0.03	2.41 ± 0.09	123.1 ± 0.5
$\frac{3}{2}$	5.66 ± 0.06	-0.75 ± 0.03	3.10 ± 0.2	132 ± 1
1.84 ± 0.02	3.24 ± 0.05	-1.34 ± 0.02	1.91 ± 0.3	120 ± 1

The fit was performed with the MINUIT-CERN minimization program, first with different fixed reasonable n values such as 1, $\frac{3}{2}$, 2 and then leaving the exponent n as a free parameter. $n = \frac{3}{2}$ and $n = 2$ are favored by the different existing theories.[2,4] The data presented in Table I are the values of the parameters obtained in the least-squares fit for $n = 2$ and $n = \frac{3}{2}$, together with their statistical error in the temperature range $2.3 < T < 22$ K. The mean-square deviations were similar in both cases. The points at the lowest temperatures were best fitted, however, by the value $n = 2$. $n = 1$ yielded a meaningfully worse fit to the data.

Other fits were tried leaving n free and changing the temperature range. Table I shows the coefficients obtained for $2.3 < T < 14.5$ K. Changing the upper limit of the temperature range affects the n value, which becomes closer to 2 when the temperature interval is made narrower.

III. DISCUSSION

A. Secondary contribution

In this paragraph we discuss the contributions to P_s' due to crystal strain. These contributions can be calculated with the available data. The room-temperature values of e_{31}, P_s, and e_{33}, taken from Ref. 12, are 23, 70, and 133 μC/cm^2, respectively. I have calculated a_j by using the Grüneisen parameters of Rao and Menon,[14] and the T^3 contribution to the heat capacity given by Lawless,[1] obtaining $a_1 = 2.94 \times 10^{-12}$ K^{-4}, $a_3 = 0.265 \times 10^{-12}$ K^{-4}. Using these values in Eq. (2) we arrive at

$$\frac{Q}{A} = P_0(O) - P_0(T) - 1.46 \times 10^{-16} T^4 \frac{\text{C}}{\text{cm}^2} \ .$$

As can be observed, the value $b = -1.57 \times 10^{-16}$ C/cm^{2}K^4 for $n = 2$ compares very well with the calculated one. The use of room-temperature values of e_{ij} is not believed to affect the comparison. As quoted in Ref. 12, these parameters have very weak temperature dependence around and above room temperature and no anomalies are expected at lower temperature. It is also worth remarking that the piezoelectric contribution to the secondary one is only 29%.

B. Primary contribution

The excellent agreement between the measured and the calculated secondary contribution supports a $P_0 \propto T^2$ dependence at the lowest temperatures, in agreement with Born's theory. In the framework of this theory, the behavior $P_0 \propto T^2$ is due to the electronic cloud deformation induced by the acoustic phonons. According to Born, when $T \ll \Theta_D$

$$P_0 = \frac{\pi^2}{6} a' \frac{T^2}{\Theta_D^2} \ , \tag{4}$$

where a' is given by the expression[15]

$$a' = \frac{9\bar{\beta}h^2}{k_B \Theta_D v_a} \ ,$$

v_a being the volume per atom, and $\bar{\beta}$ a suitable average of the second-order dipole moments of the lattice, β_{ij}.

For LiTaO$_3$, Glass and Lines[12] have obtained, using the dynamic pyroelectric technique, a small increase in p'/C below 10 K, being $p' = dP_s'/dT$ and C the heat capacity. An analysis of these data by Lines[7] in terms of the Born theory, results in a value for the primary pyroelectric coefficient

$$p_0 = -2.5 \times 10^{-11} B \left(\frac{\Theta_0}{2T} \right) \ \text{C/K cm}^2 \ ,$$

where $B(\Theta_0/2T)$ is the Born function. For LiTaO$_3$, using $\Theta_D = 450$ K, I obtain, at low temperature, $a' = -1.125 \times 10^{-14}$ C/cm^2. For LiNbO$_3$ with $\Theta_D = 560$ K, using the data of the table, $a' = -4.73 \times 10^{-15}$ C/cm^2 is obtained. From these a' values and using the expression (4), we have, for the ratio between the averaged second-order dipole moments of these materials

$$\frac{\bar{\beta}_{\mathrm{LiNbO_3}}}{\bar{\beta}_{\mathrm{LiTaO_3}}}=0.8 \ .$$

I have used 7.45 and 4.5 g/cm^3 for the densities of $\mathrm{LiTaO_3}$ and $\mathrm{LiNbO_3}$, respectively. The similar value of $\bar{\beta}$ for these substances, which are isomorphous, suggests a dominant role of the oxygen-ion deformability on the behavior of P_0 at low temperatures. It is interesting to remark that if we use the available low-temperature specific-heat data,[1] the ratio p'/C increases mainly[16] when $T \rightarrow 0$ K.

The Raman results from Penna *et al.*,[17] for the $\mathrm{LiTaO_3}$, have been used by Lines and Glass[10] for the successful interpretation of the pyroelectric response. This analysis is performed between 10 and 200 K with only two Einstein contributions, with frequencies $\nu_1 = 81$ cm^{-1}, $\nu_2 = 220$ cm^{-1} corresponding to two $A_1(T)$ optical modes, the lower one dominating the behavior up to $T \simeq 30$ K.

An extrapolation of this behavior to $\mathrm{LiNbO_3}$, which is isomorphous with the $\mathrm{LiTaO_3}$, suggests that the exponential term must correspond to the low-temperature contribution of an Einstein term coming from a polar mode of frequency near 90 cm^{-1}. However, no $A_1(T)$ optical mode at these frequencies has been reported until now from Raman,[18] infrared spectroscopy[19] or inelastic neutron scattering.[20]

Lawless[1] has obtained, from specific-heat measurements on some ferroelectric materials, a maximum on C_V/T^3 at unusually low temperatures, which has been analyzed in terms of an Einstein contribution. For $\mathrm{LiNbO_3}$, he obtains a characteristic temperature $\Theta_E = 114$ K, which compares well with the value 123.5 K reported from this experiment for $n = 2$.

IV. CONCLUSIONS

In my opinion, these measurements of P_s' yield considerable amounts of information, including the following points.

(a) The excellent agreement between measured and calculated secondary contribution supports a $P_0 \propto T^2$ dependence in agreement with the Born theory.

(b) Within the framework of this theory, a comparison has been made between $\mathrm{LiTaO_3}$ and $\mathrm{LiNbO_3}$, and we obtain similar values for the averaged second-order dipole moments, that allow us to realize the importance of the oxygen deformability on the pyroelectric behavior at lower temperatures.

(c) The comparison with $\mathrm{LiTaO_3}$ allows us to assume the existence of an $A_1(TO)$ optical mode near 90 cm^{-1}. This mode must be that responsible for the maximum on C/T^3 observed by Lawless.[1]

(d) The possibility of a $T^{3/2}P_0$ dependence at low temperatures cannot be ruled out from these measurements. But I think that the consistency of the interpretation according to the Born theory is very significant.

It would be interesting to have more data on piezoelectric compliances, specific heat, and thermal expansion at low temperatures in order to clarify this point.

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