

Influence of Critical Polarization Fluctuations on the Photoelastic Behavior of BaTiO_3

M. G. Cohen,* M. DiDomenico, Jr., and S. H. Wemple
Bell Telephone Laboratories, Murray Hill, New Jersey 07974

(Received 12 December 1969)

Measurements of the temperature dependence of the p_{11} and p_{12} elasto-optic tensor coefficients of BaTiO_3 in the cubic phase confirm the previously predicted anomalous $T/(T - T_0)^2$ enhancement caused by critical polarization fluctuations (T_0 is the Curie-Weiss temperature). The p_{11} and p_{12} data provide an estimate of the polarization-fluctuation correlation volume of $V_c = 4.5 \pm 1.2 \times 10^4 \text{ \AA}^3$, and lend strong support to the view that V_c is at most weakly temperature-dependent and does not display critical behavior.

The existence of critical polarization fluctuations near the Curie point in ferroelectrics has been inferred from a number of observations ranging from low-frequency noise measurements¹ to Raman,² neutron,³ and electron scattering experiments.⁴ It was suggested by Hofmann⁵ that mean square polarization fluctuations in the cubic phase of BaTiO_3 make a significant contribution to the refractive index via the electro-optic interaction. Recently, Wemple and DiDomenico⁶ postulated that this fluctuation contribution can be modulated by strain, and, as a result, an anomalous enhancement of the elasto-optic coefficients should occur near the Curie temperature in ferroelectrics. Using a simple thermodynamic treatment and a temperature-independent polarization fluctuation cluster volume, it was shown⁶ that the fluctuation contribution to the elasto-optic coefficients should vary with temperature as $T/(T - T_0)^2$, where T_0 is the Curie-Weiss temperature. Based on available elasto-optic data for $\text{KTa}_{0.65} \text{Nb}_{0.35}\text{O}_3$ it was concluded that the observed temperature dependence of the quantity $p_{11} - p_{12}$ was consistent with the theoretical predictions and that the cluster or correlation volume was approximately 10^5 \AA^3 . In this paper, we report results of an accurate ultrasonic determination of the p_{11} and p_{12} elasto-optic tensor coefficients in the cubic phase ($131 < T < 170 \text{ }^\circ\text{C}$) of melt-grown single crystals of BaTiO_3 . These results confirm the predicted $T/(T - T_0)^2$ temperature dependence of the polarization fluctuation contribution, provide an estimate of the correlation volume, and lend further support to the view expressed elsewhere^{4,7} that the correlation volume is at most weakly temperature dependent in displacive ferroelectrics and does not display critical behavior.

The elasto-optic coefficients were measured using an ultrasonic Bragg diffraction technique described elsewhere.⁸ In the present case, a 200-MHz longitudinal mode pulse of 200-nsec duration,

generated by a ZnO thin-film transducer, was propagated through a Z -cut crystal quartz buffer rod and into a BaTiO_3 sample along the [100] axis. The elasto-optic coefficients were determined relative to those of quartz⁹ by measuring the intensities of the 6328 \AA laser light Bragg-diffracted by the incident and reflected ultrasonic pulses in both the BaTiO_3 sample and the quartz rod. The sample-buffer rod assembly was mounted in a small oven equipped with optical windows in which the temperature could be controlled to within $0.2 \text{ }^\circ\text{C}$ up to $170 \text{ }^\circ\text{C}$. The bond between the BaTiO_3 crystal and the quartz rod was made in the oven at temperatures above the transition temperature ($T_c = 131.2 \text{ }^\circ\text{C}$ on cooling) with Nonaq stopcock grease. By polarizing the incident light beam either perpendicular or parallel to the direction of ultrasonic strain, i.e., along the [010] or [100] directions, respectively, the absolute values of the coefficients p_{12} and p_{11} were obtained separately. The magnitude and sign of the ratio p_{12}/p_{11} were determined by measuring the angle between the polarizations of the diffracted and incident beams when the incident beam was polarized at 45° to the [100] axis.¹⁰ Combining the observation that $0 < p_{12}/p_{11} < 1$ with the result that $p_{11} - p_{12} > 0$,¹¹ we conclude that both p_{11} and p_{12} are positive. In Fig. 1, we show the experimentally observed temperature dependence of p_{11} and p_{12} between 131.7 and $170 \text{ }^\circ\text{C}$. A strong increase in the vicinity of T_c is clearly evident. We now show that the observed temperature dependence of the elasto-optic coefficients can be understood using the polarization fluctuation model postulated in Ref. 6.

It is well known that in thermodynamic equilibrium the mean square polarization fluctuation in a cubic crystal is given by

$$\langle \delta P^2 \rangle = kT\epsilon^*/V_c , \quad (1)$$

where k is Boltzmann's constant, ϵ^* is the zero-strain (clamped) dielectric constant, and V_c is a

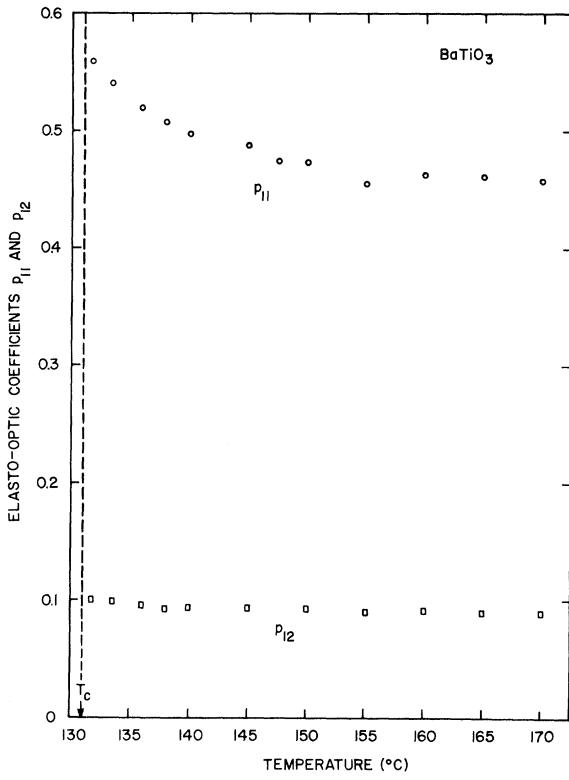


FIG. 1. Temperature dependence of p_{11} and p_{12} elasto-optic tensor coefficients of BaTiO₃ in the cubic phase. The Curie point on cooling is $T_c = 131.2^\circ\text{C}$.

correlation volume.⁴ Equation (1) essentially defines V_c . In the absence of strain, $\langle \delta P^2 \rangle$ contributes to the refractive index an amount

$$\langle \delta n \rangle = - \left\langle \frac{1}{2} n^3 \langle g^x \rangle \langle \delta P^2 \rangle \right\rangle, \quad (2)$$

where n is the refractive index and $\langle g^x \rangle$ is a suitably averaged clamped quadratic electro-optic coefficient. The fluctuation contribution given by Eq. (2) has been observed directly by Hofmann⁵ in flux-grown crystals and more recently by Singh *et al.*¹² in melt-grown BaTiO₃ crystals. In the presence of an applied strain δx_{kl} , the polarization fluctuation contribution to the elasto-optic p coefficients is given by

$$\delta p_{ijkl} = \delta \langle \delta (1/n^2) \rangle_{ij} / \delta x_{kl}. \quad (3)$$

To compute $\langle \delta (1/n^2) \rangle_{ij}$, we make the reasonable assumption that a random spatial distribution of polarization fluctuation clusters exists with each cluster having its polar axis along crystallographic <100> directions. For reasons described elsewhere,⁴ we take these clusters to be long needles of mean diameter Λ and mean length L so that $V_c \sim L\Lambda^2$. Using this model and averaging over clusters it can be shown that

$$\delta p_{11} = \frac{g_{11}^x}{(2 + L/\Lambda)} \left[1 + \frac{g_{12}^x}{g_{11}^x} \left(1 + \frac{L}{\Lambda} \right) \Delta \right] \frac{\delta \langle \delta P_1^2 \rangle}{\delta x_1} \quad (4)$$

$$\text{and} \quad \delta p_{12} = \frac{g_{12}^x}{(2 + L/\Lambda)} \left[1 + \frac{g_{11}^x}{g_{12}^x} \left(1 + \frac{g_{12}^x}{g_{11}^x} \frac{L}{\Lambda} \right) \Delta \right] \frac{\delta \langle \delta P_1^2 \rangle}{\delta x_1}, \quad (5)$$

where Δ is defined by

$$\Delta \equiv \frac{\delta \langle \delta P_2^2 \rangle / \delta x_1}{\delta \langle \delta P_1^2 \rangle / \delta x_1}, \quad (6)$$

and we have used the symmetry relation $\delta \langle \delta P_2^2 \rangle / \delta x_1 = \delta \langle \delta P_3^2 \rangle / \delta x_1$. We obtain an expression for $\delta \langle \delta P_1^2 \rangle / \delta x_1$ by differentiating Eq. (1) with respect to strain assuming that the correlation volume V_c does not change and using the Curie-Weiss law $\epsilon^x = \epsilon_0 C / (T - T_0)$, where C is the Curie constant and ϵ_0 is the free-space permittivity. Because a detailed fluctuation theory applicable to anisotropic media is not available, we consider a simple model in which polarization fluctuations normal to the strain axis are not affected by the strain, i.e., $\Delta \approx 0$. Equations (4), (6), and (1) then yield

$$\delta p_{11} = (k C \epsilon_0 g_{11}^x / V_c) (\delta T_0 / \delta x_1) \times (2 + L/\Lambda)^{-1} [T / (T - T_0)^2] \quad (7)$$

$$\text{and} \quad \delta p_{12} / \delta p_{11} = g_{12}^x / g_{11}^x. \quad (8)$$

Equation (8) provides a consistency check on the $\Delta \approx 0$ model.

To check the validity of the functional form of Eq. (7) we have plotted p_{11} versus $T / (T - T_0)^2$ in Fig. 2. The observed linear relationship strongly supports the view that polarization fluctuations give rise to the temperature-dependent elasto-optic behavior shown in Fig. 1. Furthermore, this result also provides evidence that the correlation volume does not display critical behavior and is

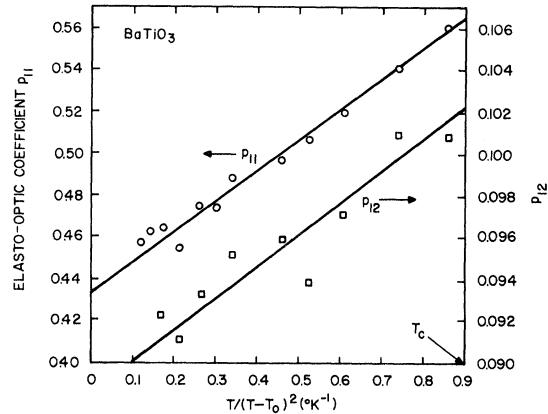


FIG. 2. Dependence of p_{11} and p_{12} elasto-optic coefficients on the quantity $T / (T - T_0)^2$ [see Eq. (7)]. The Curie-Weiss temperature in this sample is $T_0 = 110^\circ\text{C}$ (see Ref. 16).

at most weakly temperature dependent. The temperature-independent contribution to p_{11} given by the intercept in Fig. 2 has the value $p_{11}^0 = 0.43$. At $T = T_c$, the fluctuation contribution is $\delta p_{11} = 0.14$. Direct observation of p_{12} and measurement of the ratio p_{12}/p_{11} yield results for the p_{12} temperature dependence which are consistent with the $T/(T - T_0)^2$ relationship observed for p_{11} (see Fig. 2). Because of the magnitude of p_{12} (approximately 20% of p_{11}) and the smaller observed variation with temperature (see Fig. 1) the accuracy of these measurements is poorer than for p_{11} . Our best estimate for the temperature-independent component of p_{12} is $p_{12}^0 = 0.089 \pm 0.004$, and for the fluctuation component is $\delta p_{12} = 0.013 \pm 0.002$. We thus find an experimental value of $\delta p_{12}/\delta p_{11} = 0.093 \pm 0.02$. To compare this result with the prediction of Eq. (8) we require values for g_{11}^x and g_{12}^x . To our knowledge these quantities have not been measured, but they can be obtained from the known values of the zero-stress coefficients g_{11}^x and g_{12}^x by correcting for the photoelastic contribution using the relations

$$\begin{aligned} g_{11}^x - g_{11}^x &= p_{11}Q_{11} + 2p_{12}Q_{12}, \\ g_{12}^x - g_{12}^x &= p_{12}Q_{11} + (p_{11} + p_{12})Q_{12}. \end{aligned} \quad (9)$$

Taking the electrostriction coefficients¹³ $Q_{11} = 0.10m^4/C^2$ and $Q_{12} = -0.038m^4/C^2$, and the g coefficients¹⁴ $g_{11}^x = 0.12m^4/C^2$ and $g_{12}^x = -0.01m^4/C^2$, we find on substitution into Eq. (9) that $g_{11}^x = 0.072m^4/C^2$ and $g_{12}^x = 0.005m^4/C^2$. These results give $g_{12}^x/g_{11}^x \approx 0.07$. In view of the uncertainties in the magnitudes of the g^x and Q coefficients, we consider that the agreement between experimental va-

lues of $\delta p_{12}/\delta p_{11}$ and g_{12}^x/g_{11}^x is sufficient to support the validity of Eq. (8) and hence the consistency of the $\Delta \approx 0$ model.

We now calculate the correlation volume V_c using Eq. (7). It can be shown that¹⁵

$$\delta T_0/\delta x_1 = 2q_{11}\epsilon_0 C, \quad (10)$$

where $q_{11} = c_{11}Q_{11} + 2c_{12}Q_{12}$, and c_{11} and c_{12} are elements of the elastic stiffness tensor. Substituting $C = 1.8 \times 10^5$ °C,¹⁶ $T_0 = 110$ °C,¹⁶ $c_{11} = 1.73 \times 10^{11}$ N/m^2 ,¹⁷ $c_{12} = 0.82 \times 10^{11}$ N/m^2 ,¹⁷ and $L/\Lambda = 5-10$ into Eq. (7) we obtain a value

$$V_c = 4.5 \pm 1.2 \times 10^4 \text{ Å}^3. \quad (11)$$

Our choice for the aspect ratio L/Λ is based on detailed arguments given elsewhere.^{3,4} It is of interest that the magnitude of the correlation volume obtained here from photoelastic measurements is within the range 10^4-10^5 Å^3 predicted on the basis of electron scattering,⁴ bandedge temperature dependence,¹⁸ and refractive-index temperature-dependence results.^{12,18} These experiments also indicate noncritical behavior of V_c . Our experimental results lend support to the view expressed by Lines⁷ that intercell correlations are weakly temperature dependent in displacive ferroelectrics.

In conclusion, we have shown that a simple polarization fluctuation model can account for the temperature-dependent photoelastic behavior of BaTiO₃ above the Curie point. The results indicate that the correlation volume does not display critical behavior and has a value consistent with results obtained from other types of experiments.

*Present address: Quantronix Corp., Smithtown, N. Y.

¹J. J. Brophy, in *Fluctuation Phenomena in Solids*, edited by R. E. Burgess (Academic, New York, 1965), Chap. I.

²M. DiDomenico, Jr., S. H. Wemple, S. P. S. Porto, and R. P. Bauman, Phys. Rev. 174, 522 (1968); also, S. H. Wemple and M. DiDomenico, Jr., in *Light Scattering Spectra of Solids*, edited by G. B. Wright (Springer, New York, 1969), p. 65.

³Y. Yamada and G. Shirane, Phys. Rev. 177, 848 (1969).

⁴S. H. Wemple, M. DiDomenico, Jr., and A. Jayaram, Phys. Rev. 180, 547 (1969).

⁵R. Hofmann, Ph.D. thesis, Eidgenössische Technische Hochschule, Zürich, 1968 (unpublished).

⁶S. H. Wemple and M. DiDomenico, Jr., Phys. Rev. B 1, 193 (1970).

⁷M. E. Lines, Phys. Rev. (to be published).

⁸R. W. Dixon and M. G. Cohen, Appl. Phys. Letters 8, 205 (1966).

⁹H. H. Landolt and R. Börnstein, *Elastic, Piezoelectric, Piezo-optic, and Electro-optic Constants of Crystals* (Springer, Berlin, 1966), Group III, Vol. 1, p. 137.

¹⁰K. Vedam and S. Ramaseshan, in *Progress in Crystal Physics*, edited by R. Krishnan (Interscience, New York, 1958).

¹¹This result is obtained by noting that the difference between unclamped and clamped quadratic electro-optic coefficients $g_{11} - g_{12}$ is positive. See A. R. Johnston, Appl. Phys. Letters 7, 195 (1965). $Q_{11} - Q_{12}$ is also positive; see Ref. 13.

¹²S. Singh, S. H. Wemple, M. DiDomenico, Jr., J. Potopowicz, and I. Camlibel (unpublished).

¹³P. Joho, Z. Krist. 120, 329 (1964).

¹⁴E. P. Ippen, IEEE J. Quantum Electron. QE-2, 152 (1966).

¹⁵See, for example, F. Jona and G. Shirane, *Ferroelectric Crystals* (Macmillan, New York, 1962), pp. 144-145.

¹⁶S. H. Wemple, M. DiDomenico, Jr., and I. Cam-

libel, J. Phys. Chem. Solids **29**, 1797 (1968); also I. Camlibel, M. DiDomenico, Jr., and S. H. Wemple, *ibid.* (to be published).

¹⁷D. Berlincourt and H. Jaffe, Phys. Rev. **111**, 143 (1958). The c_{11} value is confirmed by this study.

¹⁸S. H. Wemple (unpublished).

Temperature and Field Dependence of the Weak Ferromagnetic Moment of Hematite*

C. W. Searle and G. W. Dean

Department of Physics, University of Manitoba, Winnipeg 19, Canada

(Received 3 October 1969)

Deviations from the expected temperature dependence of the weak magnetic moment m are explained by considering the microscopic differences between the dipole-dipole and single-ion contributions to the anisotropy energy.

INTRODUCTION

Hematite (α Fe₂O₃) is a well-known antiferromagnet with a rhombohedral crystal structure. It also possesses a weak spontaneous magnetization. With cooling it is found that there exists a certain temperature T_M , at which the spontaneous magnetization suddenly disappears.¹ Below T_M the antiferromagnetic axis coincides with the [111] direction, while above T_M the antiferromagnetic axis is in the (111) plane.² The origin of the weak ferromagnetic moment is due to the Dzialoshinskii-Moriya (DM) interaction^{3,4} which results in a slight canting of the sublattice magnetizations to produce a weak ferromagnetic moment. The expression for the Hamiltonian in the molecular field (MF) approximation is usually written as⁵

$$\epsilon = \lambda \vec{M}_1 \cdot \vec{M}_2 - \vec{D} \cdot (\vec{M}_1 \times \vec{M}_2) - \vec{H} \cdot (\vec{M}_1 + \vec{M}_2) + \epsilon_K, \quad (1)$$

where \vec{M}_1 and \vec{M}_2 are the sublattice magnetizations, λ is the MF constant, \vec{D} is the DM vector and is parallel to the [111] direction, \vec{H} is the applied field, and ϵ_K represents the anisotropy energy.

Searle⁶ has recently suggested, using symmetry arguments, that once the spins have been labeled according to their respective sublattices the sense of \vec{D} along the [111] direction is still undetermined. This then leads to the possibility of observing ferromagnetic domains which would not be associated with antiferromagnetic domains.⁷ This does not rule out the existence of ferro- and antiferromagnetic domains reported by Nathans *et al.*⁸ It was also stressed that \vec{D} should be replaced by $\langle \vec{D} \rangle$, where $\langle \dots \rangle$ means the appropriate statistical average. The expression for the weak magnetic moment m can then be written as

$$m = (\langle H_D \rangle / H_e) M. \quad (2)$$

Here $\langle H_D \rangle = \langle D \rangle M$, M is the magnitude of one of the

sublattice magnetizations, and $H_e = \lambda M$. Equation (2) implies that the ratio $m/M = \langle D \rangle / \lambda$ should decrease with increasing temperature. It was also suggested that the field-induced transition, for temperatures below T_M , might be described better using this statistical model than the usual MF approach where \vec{D} is assumed to be constant (such as in calculations by Cinader and Shtrikman⁹). The purpose of this experiment was to look for some of these effects using static magnetization measurements.

RESULTS

The upper curve in Fig. 1 indicates the temperature dependence of the normalized sublattice magnetization, M/M_0 . Values of M/M_0 are taken from

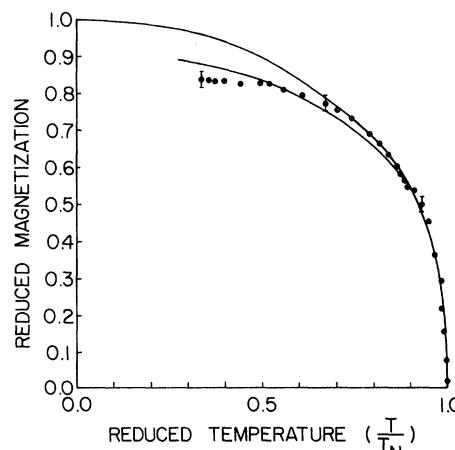


FIG. 1. Temperature dependence of the weak ferromagnetic moment of hematite. The upper curve represents the normalized temperature dependence of the sublattice magnetization, M/M_0 , the dots are the experimental data m/m_0 , while the lower curve is calculated from Eq. (6).