Influence of Critical Polarization Fluctuations on the Photoelastic Behavior of $BaTiO_3$

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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 $V_c = 4.5 \pm 1.2 \times 10^4$ Å^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 measurements[1] to Raman,[2] neutron,[3] and electron scattering experiments.[4] It was suggested by Hofmann[5] 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 DiDomenico[6] 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 shown[6] 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 $KTa_{0.65}Nb_{0.35}O_3$ 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 Å^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 ($131 < T < 170$ °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 quartz[9] by measuring the intensities of the 6328 Å 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 °C up to 170 °C. The bond between the $BaTiO_3$ crystal and the quartz rod was made in the oven at temperatures above the transition temperature ($T_c = 131.2$ °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 °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

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

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

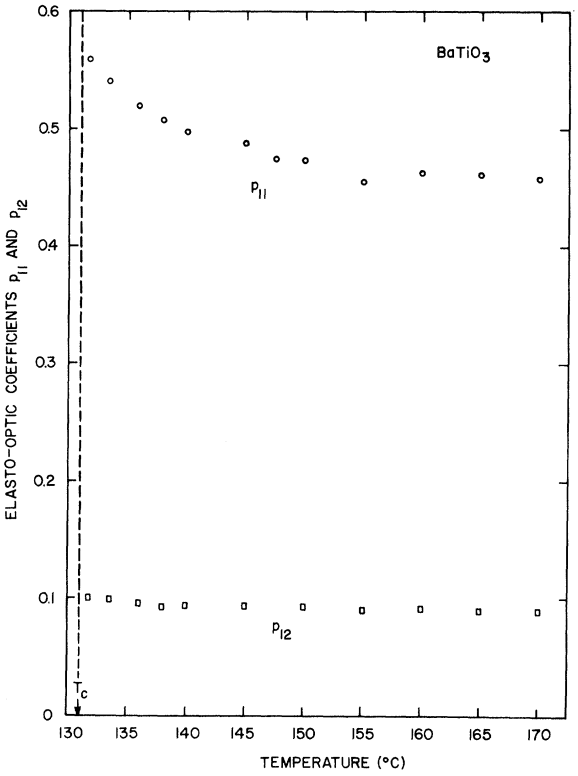

FIG. 1. Temperature dependence of p_{11} and p_{12} elasto-optic tensor coefficients of $BaTiO_3$ in the cubic phase. The Curie point on cooling is $T_c = 131.2°C$.

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

$$\langle \delta n \rangle = -\langle \tfrac{1}{2} n^3 \rangle \langle g^x \rangle \langle \delta P^2 \rangle \ , \tag{2}$$

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 Hofmann[5] in flux-grown crystals and more recently by Singh *et al.*[12] in melt-grown $BaTiO_3$ crystals. In the presence of an applied strain δx_{kl}, the polarization fluctuation contribution to the elasto-optic p coefficients is given by

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

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

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

and

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

where Δ is defined by

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

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

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

and

$$\delta p_{12} / \delta p_{11} = g_{12}^x / g_{11}^x \ . \tag{8}$$

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

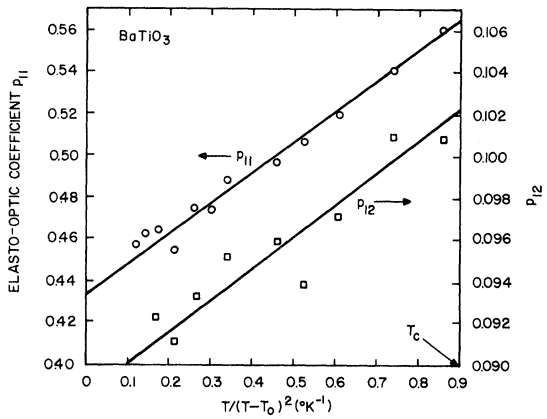

FIG. 2. Dependence of p_{11} and p_{12} elasto-optic coefficients on the quantity $T/(T - T_0)^2$ [see Eq. (7)]. The Curie-Weiss temperature in this sample is $T_0 = 110\,°C$ (see Ref. 16).

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

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

Taking the electrostriction coefficients[13] $Q_{11} = 0.10 m^4/C^2$ and $Q_{12} = -0.038 m^4/C^2$, and the g coefficients[14] $g_{11}^X = 0.12 m^4/C^2$ and $g_{12}^X = -0.01 m^4/C^2$, we find on substitution into Eq. (9) that $g_{11}^x = 0.072 m^4/C^2$ and $g_{12}^x = 0.005 m^4/C^2$. 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 values 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 that[15]

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

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

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

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 Lines[7] 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 $BaTiO_3$ 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.

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

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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 Fe_2O_3) 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 as[5]

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

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.

Searle[6] 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 $\langle \cdots \rangle$ 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 Shtrikman[9]). 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

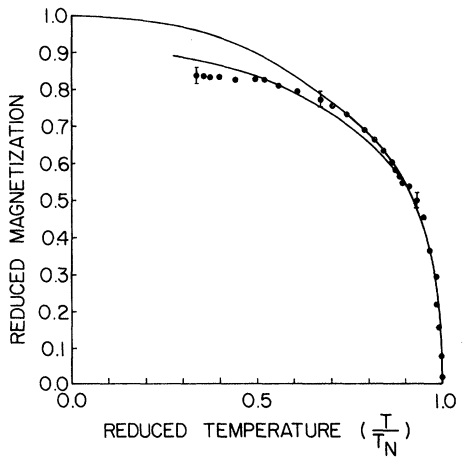

FIG. 1. Temperature dependence of the weak ferromagnetic moment of hematite. The upper curve represents the normalized temperature dependence of the sublattice magnetization, M/M_0, the dots are the experimental data m/m_0, while the lower curve is calculated from Eq. (6).