Crystal optical studies of precursor and spontaneous polarization in PbTiO$_3$

W. Kleemann and F. J. Schäfer

Laboratorium für Angewandte Physik, Universität Duisburg, D-4100 Duisburg 1, Federal Republic of Germany

D. Rytz

Hughes Research Laboratories, Malibu, California 90265

(Received 2 April 1986)

High-resolution measurements of the cubic refractive index (RI) of PbTiO$_3$ reveal contributions due to the fluctuating polarization, which attains about 14% of the spontaneous polarization at $T_c = 769$ K. In the tetragonal phase the anomalies of both RI's are shown to be negative with nearly equal amplitude. The nearly vanishing optical anisotropy can be understood in terms of the crystal optical contributions due to tetragonality and to the spontaneous Kerr effect, respectively. A slight nonproportionality of the RI's causes the well-known anomalous temperature dependence of the linear birefringence exhibiting a maximum at 670 K. No evidence is found for another phase transition at low temperatures.

I. INTRODUCTION

Lead titanate PbTiO$_3$ undergoes a first-order phase transition at $T_c \sim 765$ K,[1] which "appears to be a textbook example of a displacive ferroelectric transition."[2] In particular the soft mode associated with the cubic-to-tetragonal lattice distortion is underdamped as evidenced by Raman[3] and neutron scattering[4] experiments. Owing to the large order-parameter discontinuity at T_c, any crossover into an order-disorder regime[5] seems to be absent. It seems, hence, to differ from other ferroelectric perovskites like BaTiO$_3$, where polarized precursor clusters have been shown to exist well above T_c and to produce a characteristic anomaly of the optical refractive index (RI), n.[6] For PbTiO$_3$, however, within their experimental accuracy, $\delta n \sim 10^{-4}$, Burns et al.[7] do not find any hint at deviations from the classical linear temperature dependence of $n(T)$. Qualitatively one might argue that the first-order transition occurs before correlated fluctuations set in.[7] Alternatively we recently proposed[8] that the δn effect in PbTiO$_3$ might just be diminished, e.g., by competing contributions to $n(T)$ due to hard lattice modes. Nevertheless, a small, but finite effect should be observable at higher resolution keeping in mind the rather general correspondence between the order-parameter autocorrelation function, $\langle \delta P^2 \rangle$, and the index anomaly $\delta n(T)$.[8] In this paper we shall show, indeed, its very existence. Owing to the high resolution of our interferometric measurements[9] it can clearly be resolved, although its value at T_c is one order of magnitude smaller than that of BaTiO$_3$ (Ref. 6) and KNbO$_3$,[8] respectively.

Another aim of this work is to critically check the temperature dependence of the linear birefringence (LB), Δn_{ac}, within the tetragonal ferroelectric phase. It is surprising that the data reported up to now by different authors[10−13] do not coincide with one another. The only clear common feature is the unusual temperature dependence of the LB, peaking at about 670 K and decreasing on lowering the temperature. Different absolute values of Δn_{ac} found by different authors may hint at problems in properly selecting single domains. Our higher-precision equipment[9] encouraged us to tackle this problem anew. Indeed, somewhat larger absolute values of Δn_{ac} than hitherto reported seem to hint at more complete single-domain selection.

The anomalous temperature dependence of Δn_{ac} has been discussed by quite a number of authors. Känzig[14] initially proposed that a saturation effect of the internal field might be the reason for the low-T drop of Δn_{ac}. However, according to measurements of P_s by Venevtsev et al.[15] and to calculations of the ionic displacements emerging from neutron powder diffraction data,[16] the spontaneous polarization seems rather to increase with decreasing temperature than to saturate or even to decrease. Later on, the spectroscopical model of DiDomenico and Wemple[17] has attracted a lot of interest. However, neither the treatment of Thacher[18] nor that of Singh et al.[19] can finally explain the microscopic origin of the decrease of Δn_{ac} at low T. Both depend on a phenomenological dispersion constant K having an unexplained detrimental T dependence. A promising microscopic approach to the problem seems to be given by the vibronic theory of Kristofel and Gulbis.[20] It takes into account the vibronic renormalization of the transition energies between the valence and the conduction bands, which are involved in the optical permittivity tensor. A delicate balance between the linear T shift of the bare band gap and a P_s^2 dependence of its renormalization due to the interband electron-phonon coupling seems to be responsible for the anomalous T dependence of Δn_{ac}. The comparatively large P_s values seem to diminish the differences between the permittivity components ϵ_c and ϵ_a at low temperatures. Despite the success of the calculations,[20] which qualitatively yield the correct T dependence of Δn_{ac} and its dispersion, they undoubtfully bear model character and require adjustable parameters for fitting.

It may, hence, be justified to look for a proper macroscopic description of the LB. Evidently the standard formula

$$\Delta n_{ac} = -(n_0^3/2)(g_{11}^F - g_{12}^F)P_s^2 , \qquad (1)$$

where n_0 is the RI in the paraelectric phase taken at T_c, is leading to unconventional temperature-dependent stress-free P-optical coefficients g_{ij}^F.[18] Fousek and Petzelt[21] proposed to extend Eq. (1) by P_s^4 or P_sQ terms, where Q is a hard mode of the same symmetry as the order parameter. However, in a less sophisticated way Mabud and Glazer[11] were successful in explaining the unusual T dependence of Δn_{ac} by simply decomposing the LB into its electro- and elasto-optical contributions. Setting

$$\Delta n_{ac} = -(n_0^3/2)[(g_{11}-g_{12})P_s^2 + (p_{11}-p_{12})(u_{3s}-u_{1s})] , \qquad (2)$$

where g_{ij} are the clamped P-optical coefficients, p_{ij} = elasto-optic coefficients, and u_{js} = spontaneous strains in j direction, one may account for the individual temperature dependence of $P_s(T)$ and $u_{js}(T)$, respectively. Using the P_s data of Remeika and Glass[22] and their own x-ray u_{js} data, Mabud and Glazer[11] were able to qualitatively describe their $\Delta n_{ac}(T)$ curve with constant coupling coefficients. As has been suspected already by Lawless,[23] both contributions are opposite in sign and slightly nonproportional. In this paper we shall reexamine Eq. (2), which was originally suggested by Pockels.[24] Inserting improved recent $P_s(T)$ data[25] and our LB results, however, the fit with Eq. (2) is less successful and its very applicability must be cast in doubt anew.

This view is strongly supported by our new measurements of the temperature dependence of the RI's, $n_a(T)$ and $n_c(T)$. It will be shown that their anomalies, $\delta n_a(T)$ and $\delta n_c(T)$, due to the phase transition are both negative and nearly equal in amplitude. Hence, $g_{11}^F \sim g_{12}^F$ in sharp contrast with the situation found for $BaTiO_3$.[26] Thus $PbTiO_3$ remains optically nearly isotropic in its distorted phase. This is certainly due to the strong contributions of the Pb—O bonds to its polarizability. The results will be discussed in the spirit of Kinase's theory of double refraction,[27] which distinguishes different mechanisms, one being the change of dipole interaction due to the lattice deformation, another being the spontaneous Kerr effect due to the local field exerted by the spontaneous polarization. It will be shown, however, that simple proportionalities with P_s^2 and/or the spontaneous strains cannot explain the shapes of the $\delta n_a(T)$ and $\delta n_c(T)$ curves. As proposed,[21] higher-order perturbations must be included in order to describe delicate temperature dependences like that of $\Delta n_{ac}(T)$.

Some efforts have been put into looking for evidence of an additional phase transition at low temperatures. In agreement with Remeika and Glass[22] and Mabud and Glazer,[11] but contrary to Kobayashi et al.,[13] we do not find any anomaly at their $T_{c2} = 183$ K. A thorough search at lower temperatures was not successful as well. Since crystal growth of $BaTiO_3$ frequently utilizes flux materials like UO_3 (Ref. 22) or B_2O_3,[13] the incorporation of impurities cannot be excluded. These may account for the different behavior of samples from various origins.

II. EXPERIMENTAL PROCEDURE

Single crystals of $PbTiO_3$ have been prepared by the top-seeded solution growth method using PbO as a solvent. Samples with {100} faces and dimensions of approximately $2 \times 2 \times 0.5$ mm^3 were cut and polished to be optically flat within less than about 5λ over the large faces ($\lambda \sim 0.6$ μm). The samples are highly transparent at wavelengths above the absorption edge ($\lambda \sim 440$ nm for $T = 295$ K), the latter giving rise to a yellowish color (Fig. 1). On lowering the temperature, the edge shifts to shorter wavelengths thus suggesting its intrinsic nature. Some extrinsic absorption with flat spectral response due to impurities may, however, not be neglected, since the apparent optical density is higher than expected from pure reflection losses. At $\lambda = 630$ nm we measure $\log_{10}(I_0/I) = 0.31$ which is significantly larger than $-\log_{10}T = 0.19$, where $T = 2n/(n^2 + 1)$, with $n = 2.7$ (Ref. 19) is the transmission corrected for multiple reflections at both surfaces. Some of the excess optical density may be due to scattering at ferroelectric domain boundaries.

Linear birefringence and optical retardation measurements have been performed using a computer-controlled modulation method, which was described in detail elsewhere.[9] Much care was taken to select true tetragonal single domains in the room-temperature phase. It was noticed that the domain structure may be affected by the polishing procedure owing to ferroelectric interaction. In favorable cases it was possible to detwin stacked configurations of ac domains applying surface shear along c. Most of the experiments done in the tetragonal phase were finally carried out on one perfect single domain with thickness $l = 0.34$ mm. Only for the search for the predicted tetragonal-to-orthorhombic phase transition[13] was an ab domain (c axis perpendicular to the surface) selected. All measurements were done on a microscopically selected, fixed sample area of $(100 \times 100$ μm)^2 at light wavelengths of 589.3 and 632.8 nm, respectively. Temperatures between 4.5 and 100 K were achieved via
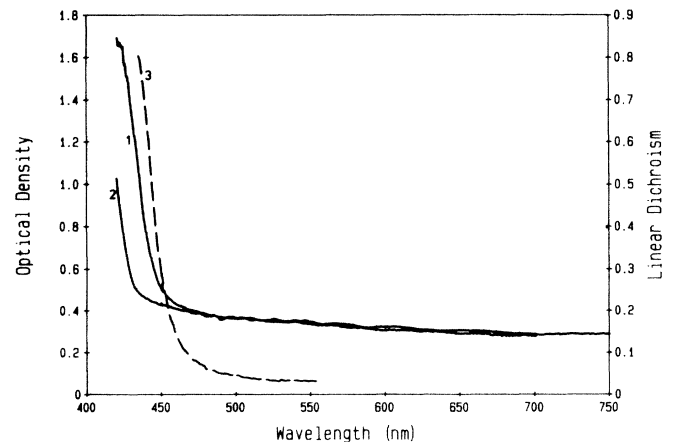

FIG. 1. Optical-absorption spectra of $PbTiO_3$ taken at 295 K (curve 1) and 5 K (curve 2), respectively, and linear dichroism measured on a single domain at 295 K (curve 3).

helium exchange gas in a cryostat and an oven, respectively. The absolute-temperature uncertainty was less than 0.5 K in all cases.

Optical transmission and linear dichroism measurements were performed using the same apparatus as for crystal optics. For spectral characteristics an $f=0.25$ m double monochromator and a halogen-tungsten lamp were attached to the microscope.

III. EXPERIMENTAL RESULTS

A. Linear birefringence

Figure 2 shows the temperature dependence of the ac birefringence, Δn_{ac}, measured at $\lambda=589.3$ nm between 4.5 and 800 K. Characteristically as in all previous investigations[10−13] there is a large jump, $\delta\Delta n_{ac}=1.5\times10^{-2}$, at $T_c=772.5$ K (on heating) and 765.0 K (on cooling). Furthermore, a broad peak arises around 670 K ($\Delta n_{max}=2.0\times10^{-2}$), followed by a continuous drop to $\Delta n_{ac}=7.5\times10^{-3}$ at low temperatures. Even at very low temperatures we do not find evidence of a second phase transition. Especially the sharp kink of Δn_{ac} found by Kobayashi et al.[13] at $T=183$ K is safely absent. Slight ($\Delta n_{ab}\sim10^{-6}$) and irregularly occurring fluctuations of the in-plane LB can unambiguously be traced back to temperature-dependent stress of multidomain samples.

It seems worthwhile to report on the difficulty to determine the absolute value of Δn_{ac} owing to the discontinuity at T_c. Since our compensation method[9] is insensitive with respect to any multiples of λ occurring in the optical path difference, an additional measurement is required to remove this ambiguity. In a previous investigation of the LB in KNbO₃ (Ref. 8) we simply measured the optical transmission of an ac sample between crossed polarizers as a function of the wavelength. Two adjacent wavelengths providing minimum transmission, λ_{N-1} and λ_N, were immediately used to calculate $\Delta n_N=\Delta n(\lambda_N)$,

$$\Delta n_N=(1/\lambda_N-1/\lambda_{N-1})^{-1}(1/l) . \quad (3)$$

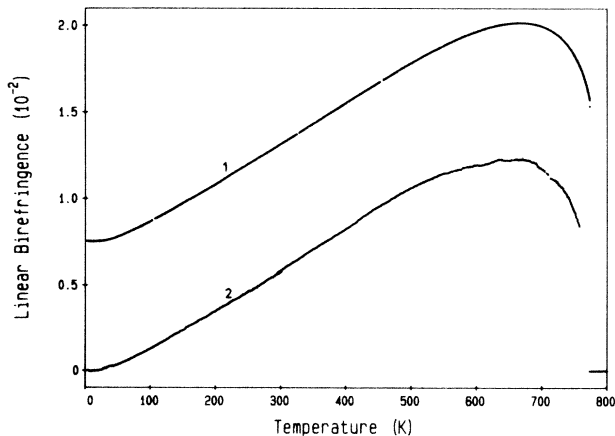This formula, however, fails in the presence of appreciable

dispersion, $\Delta n=\Delta n(\lambda)$, and must be replaced by the correct relation

$$\Delta n_N=(1/\lambda_N-1/\lambda_{N-1})^{-1}$$
$$\times[1/l-(\Delta n_N-\Delta n_{N-1})/\lambda_{N-1}] . \quad (4)$$

In the case of PbTiO₃ the error induced by Eq. (3) can be estimated[19] to be as large as about 50%. Lacking exact dispersion data, however, Eq. (4) becomes useless and had to be abandoned. Instead of a theoretical dispersion formula of the Cauchy-Sellmaier type was introduced,

$$\Delta n_N=a+b/\lambda_N^2 . \quad (5)$$

Together with the interference condition for the minima, which are well defined also in the case of PbTiO₃ (Fig. 3),

$$\Delta n_N=N\lambda_N/l \quad (6)$$

the unknown integers N are readily found from a cubic function of $1/\lambda_N$,

$$N=al/\lambda_N+bl/\lambda_N^3 . \quad (7)$$

Inserting λ_N^{-1} values from Fig. 3 together with an appropriate set of integers $\{N\}$ under the additional constraint $N(\lambda_N^{-1}=0)=0$ the parameters a and b were found by a best-fit procedure.

Figure 4 shows $1/\lambda_N$ versus N interpolated by the best-fit curve referring to $a=-1.42\times10^{-7}$ and $b=4.65\times10^{-15}$ m². $\{N\}$ starts with $N=5$ at $\lambda=690$ nm. We thus obtain $\Delta n(589.3$ nm$)=1.34\times10^{-2}$, which is used to fix the position of the LB curve in Fig. 2 at $T=295$ K. For comparison with previous work[10−13] one should consider $\Delta n(632.8$ nm$)=1.16\times10^{-2}$, which exceeds all former data, the value 1.02×10^{-2} of Shirane et al.[10] being closest to ours. Presumably lack of true single domains in the former work is responsible for the differences. Even with a polarizing microscope as used by most authors,[10−13] stacked domain configurations (Sec. II) may easily be mistaken as single domains. It should be noted that the dispersion relation (5) resembles that obtained from vibronic theory[20] except near the band gap

FIG. 2. Temperature dependence of the tetragonal birefringence, Δn_{ac}, measured on a single domain of PbTiO₃ (curve 1), in comparison with the difference $(\phi_a-\phi_c)/l$ (curve 2) of the optical retardations for a and c polarized light, respectively (see Fig. 5).
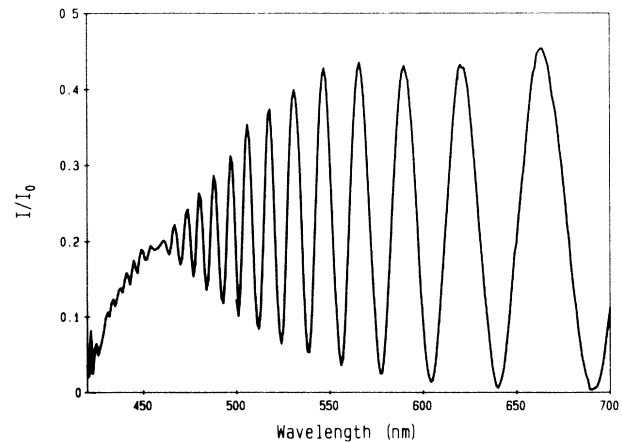

FIG. 3. Optical transmission spectrum of a single domain of PbTiO₃ at 295 K placed between crossed polarizers with its principal axes under 45° with respect to the E vector of the incident light. Sample thickness: $l=0.34$ mm.
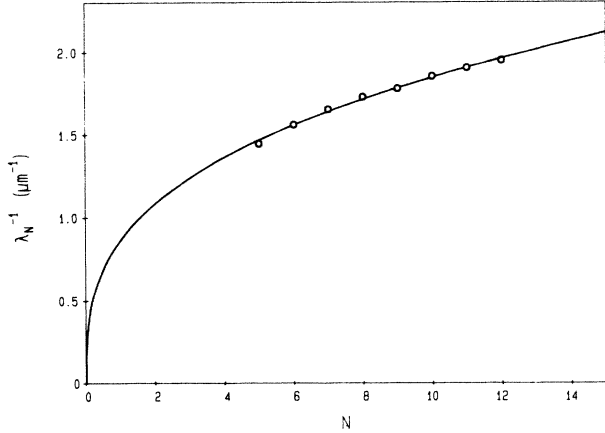
FIG. 4. Inverse wavelengths, λ_N^{-1}, for minimum transmission between crossed polarizers (see Fig. 3) plotted vs the order N of full-wavelength retardation and best fitted by a solid line according to Eq. (7).

FIG. 5. Temperature dependences of the specific optical retardations, ϕ_a/l (curve 1) and ϕ_c/l (curve 2), along the b axis of a single domain of PbTiO$_3$, arbitrarily set zero at $T=0$, curve 2 smoothly merging into ϕ/l of the cubic phase.

($\lambda < 500$ nm), where Eq. (5) becomes a poor approximation.

It is interesting to note that the contrast of the interference pattern in Fig. 3 fades out with decreasing wavelength. This is due to dichroic reflection losses at the surfaces and to dichroic absorption in the bulk. Both effects are unbalancing the amplitude ratio of the ordinary and the extraordinary rays after passing the sample, thus causing a rotation of the emerging light vector. Whereas the transmittance difference due to dichroic reflection, $| T_o - T_e |_{\text{refl}} = 2\Delta n/(n^2+1)$, amounts to only 4.5×10^{-3} at $\lambda = 500$ nm, the total dichroism (Fig. 1, curve 3) contributes with 5×10^{-2}. Taking into account an average transmission $T = 0.4$ (Fig. 1) one easily calculates $I/I_0 = 0.07$ for the minimum transmission in the crossed polarizer configuration. This is in rough agreement with the experimental data (Fig. 3). Below 450 nm the interference fringes gradually fade out owing to strong band-edge absorption.

B. Optical retardation and refractive index measurements

Figure 5 shows the optical retardations

$$\delta\phi/l = \delta n + (n-1)(\delta l/l) \tag{8}$$

measured with $\lambda = 589.3$-nm light for the ordinary (curve 1) and the extraordinary ray (curve 2), respectively, both transmitting through an ac domain along the b direction. Arbitrarily we have set $\phi_a l(0) = \phi_c/l(0) = 0$. This presentation allows one to visualize that both curves have slightly different curvatures. Their largest difference arises near 670 K as is well known from the peculiar shape of the LB curve (Fig. 2). Indeed, according to Eq. (8), the difference of the curves 1 and 2 of Fig. 5 is just the LB, $n_a - n_c$, arbitrarily set to zero at zero temperature. This is displayed as curve 2 in Fig. 2. It is seen that both Δn_{ac} (curve 1) and $(\phi_a - \phi_c)/l$ (curve 2) have the same temperature dependence, the latter one exhibiting slightly more noise as is typical for the interferometric measurement of
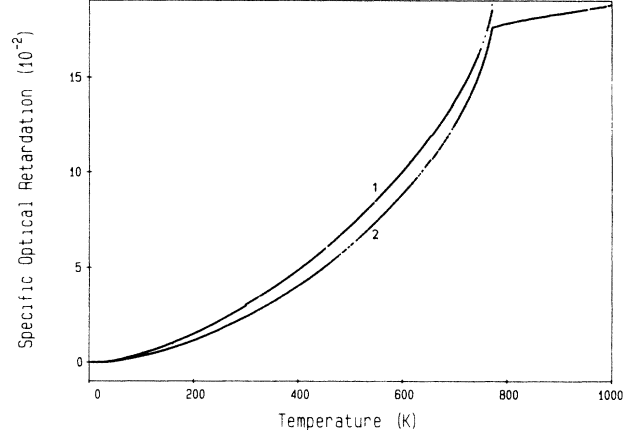
optical retardation.[9] The expected jump of ϕ/l at $T_c \sim 770$ K is not seen in Fig. 5, which shows ϕ_c/l smoothly connected at T_c with ϕ/l of the cubic phase. As discussed already in Sec. III A the determination of any retardation discontinuity of more than one wavelength requires additional data as will be outlined below.

In order to transform the curves of Fig. 5 into a plot of RI versus T, the following procedures were applied: (i) subtraction of the dilation terms $(n-1)(\delta l/l)$ in Eq. (8) using $n=2.95$ (Ref. 7) and $(da/dT)/a = 5 \times 10^{-6}$ (Ref. 13) for $T_c < T < 1000$ K, $n = 2.69$ (Ref. 19) and $(da/dT)/a = 1.25 \times 10^{-5}$ (Ref. 13) for 300 K $< T < T_c$ and a smooth $a(T)$ curve[13] below 300 K, respectively; (ii) attribution of absolute values to the resulting curves by setting $n(1000$ K$) = 2.9523$,[7] $n_a(300$ K$) = 2.697$,[19] and $n_c(300$ K$) = n_a(300$ K$) - \Delta n(300$ K$) = 2.684$, with $\Delta n(300$ K$) = 0.0134$ (Fig. 2). Figure 6 shows the resulting RI versus T curves. Now they clearly exhibit large jumps at T_c: $\delta n_a = -0.094$ and $\delta n_c = -0.111$. Furthermore it is evident that both δn_a and δn_c vary by nearly the same
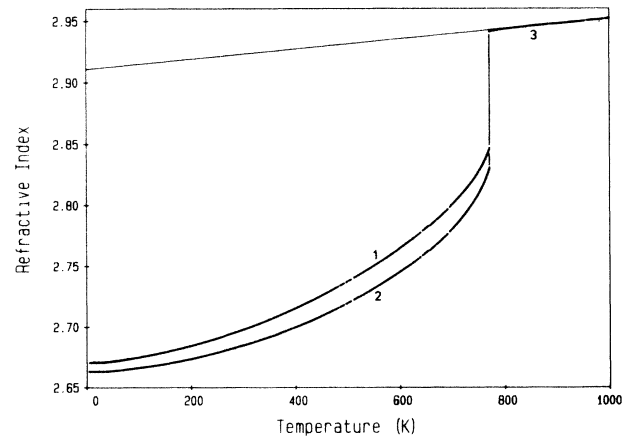

FIG. 6. Temperature dependences of the refractive indices n_a (curve 1), n_c (curve 2), and n (curve 3) of PbTiO$_3$ in its tetragonal and cubic phases, respectively.

amount into the same direction. This proves nearly isotropic electro-optical response despite the large tetragonal deformation coupled with a large spontaneous polarization found for PbTiO₃. This is quite different from BaTiO₃, where δn_a and δn_c are also both negative, but differ by more than a factor of 2.[28]

In a first attempt to describe the RI anomalies one might use the standard perturbation approach involving the free P-optical coefficients g_{ij}^F,

$$\delta n_{a,c} = -(n_0^3/2)g_{12,11}^F P_s^2 . \tag{9}$$

The expected proportionality between δn and P_s^2 should be evident from a common plot versus T. This is done in Fig. 7, where $|\delta n_{a,c}|$ are taken from Fig. 6, subtracting a linear baseline, curve 3, obtained by extrapolating n (900 K $< T <$ 1000 K) down to zero temperature. The values of $P_s^2(T)$ in the range 300 K $< T < T_c$ are taken from Bergman et al.[25] and essentially agree with those of Venevtsev et al.[15] It is evident that Eq. (9) involving constant coefficients g_{ij} totally fails. The rise of $P_s^2(T)$ below T_c is much steeper than that of both $\delta n(T)$ curves, even in the case where their discontinuities at T_c would need major corrections. Evaluating Eq. (9) by setting $n_0 = 2.93$ one formally obtains (g_{11}^F, g_{12}^F) $(T_c) = (0.043, 0.037)$ m⁴ C⁻² and (g_{11}^F, g_{12}^F) (300 K) $= (0.029, 0.027)$ m⁴ C⁻², respectively. Hence, both the coefficients and their differences, $g_{11}^F - g_{12}^F$, seem to vary with T as was stated by Thacher previously.[18] We shall recall this puzzling problem again in Sec. IV.

At this point attention should be drawn to the temperature dependence of the cubic RI. Figure 8 shows an enlarged plot of the range $T_c < T <$ 1000 K with the optical retardation ϕ/l (curve 1) measured at $\lambda = 632.8$ nm, $n(T)$ (curve 2) as calculated from ϕ/l by correcting for the lattice dilation (see above), and a linear background curve $n_0(T)$ extrapolating $n(T)$ from the range 950 K $< T <$ 1000 K down to T_c (curve 3). As expected[8] a refractive index anomaly $\delta n(T) = n_0(T) - n(T)$ arises similar to that found in BaTiO₃ (Ref. 6) and KNbO₃.[8] However, in agreement with the Burns et al.[7] supposition the tail

FIG. 8. Temperature dependences of the optical path difference $[\phi(T) - \phi(1000 \text{ K})]/l$ (curve 1), of the refractive index, $n(T) - n$(1000 K) (curve 2), and of the linear background, $n_0(T) - n$(1000 K) (curve 3), fitted to $n(T)$ at 950 K $< T <$ 1000 K.

is much smaller than in the latter cases. This explains why it remained undetected in the previous experiment.[7]

IV. DISCUSSION

A. Precursor polarization

As discussed recently[8] the RI anomaly, δn, due to precursor polarization can be described in terms of the autocorrelation function $\langle P^2 \rangle$ of the polarization,

$$\delta n(T) = (n_0^3/6)(g_{11}^F + 2g_{12}^F)\langle P^2(T) \rangle . \tag{10}$$

On the other hand $\langle P^2 \rangle$ may be described within the Ornstein-Zernike approximation by

$$\langle P^2(T) \rangle = (k_B T \epsilon \epsilon_0 q_m)[1 - \tan^{-1}(\xi q_m)/(\xi q_m)]$$
$$\times (2\pi^2 \xi^2)^{-1} . \tag{11}$$

In this expression $\epsilon \xi^{-2}$ is essentially constant.[8] Hence, one arrives at

$$\delta n(T) = c_0 T[1 - \tan^{-1}(\xi q_m)/(\xi q_m)] , \tag{12}$$

where c_0 is a constant, q_m refers to the maximum wave number of the polarization fluctuations, and $\xi = \xi_0 t^{-\nu}$ is the correlation length $(t = T/T_0 - 1, \nu \sim 0.7)$.

Figure 9 shows the fit of $\delta n(T)$ (curve 1) to the expression (12) (curve 2) using data points within $0.09 < t < 0.11$ as indicated by vertical dashed lines. $T_0 = 722$ K was chosen as the extrapolated divergence temperature of ϵ and ξ.[4] The fit is excellent with a reasonable value of $\xi_0 q_m = 0.17$. Minor deviations arise only above 920 K. They are presumably due to the subtraction procedure of $n_0(T)$, which implies the absence of any nonlinear contribution $\delta n(T)$ above 950 K. Our fit, however, strongly indicates that the fluctuation tail persists even at 1000 K: δn(1000 K) $= 0.52 \times 10^{-3}$. Taking this into account (Fig. 9, right-hand scale) we obtain the anomaly at T_c, $\delta n(T_c) = 2.25 \times 10^{-3}$. This value is only about 10% of that found for KNbO₃.[8] It may be used to estimate
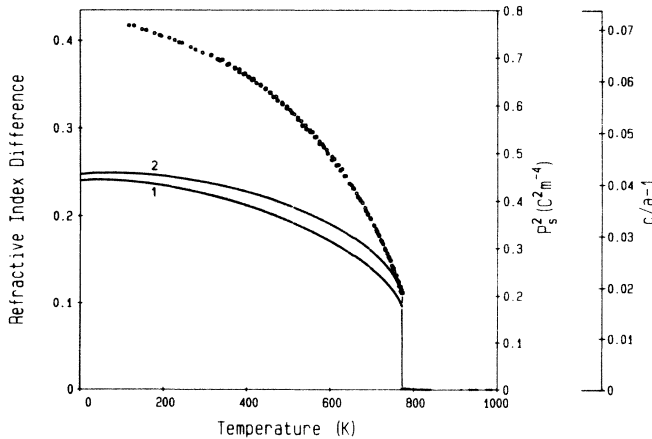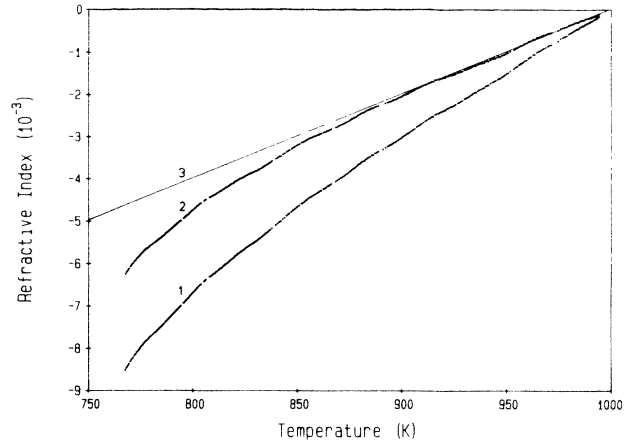

FIG. 7. Temperature dependences of the refractive index anomalies $|\delta n_a|$ and $|\delta n_c|$ (curves 1 and 2, respectively), in comparison with $c/a - 1$ (open circles) (Ref. 16) and P_s^2 (full circles) (Ref. 25).
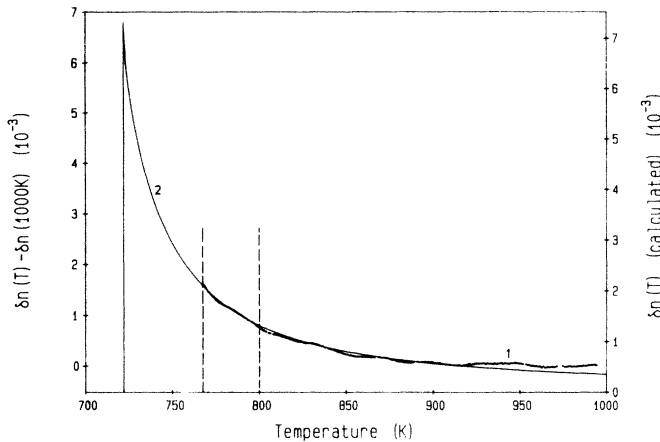
FIG. 9. Cubic refractive index anomaly of $PbTiO_3$, obtained, respectively, by subtracting curves 2 and 3 of Fig. 8, $\delta n(T) - \delta n(1000 \text{ K})$ (dotted curve 1, left-hand scale), and by fitting the δn data between 788 and 800 K (vertical dashed lines) to the Ornstein-Zernike expression (12), $\delta n(T)$ (solid curve 2, right-hand scale).

the amount of fluctuating polarization at T_c by using Eq. (10), with $n = 2.94$ (Fig. 6) and $(g_{11}^F, g_{12}^F)(T_c)$ as given above: $\langle P^2(T_c) \rangle = 0.0042$ $C^2 m^{-4}$ and, hence, $\langle P^2(T_c) \rangle^{1/2} = 0.065$ Cm^{-2}. The latter value constitutes only 14% of $P_s(T_c)$ (Ref. 25) thus indicating that the phase transitions of $PbTiO_3$ is, indeed, predominantly of the displacive type.

B. Polarization-optical properties of the tetragonal phase

A very intuitive view for analyzing the electro- and polarization-optical properties of ferroelectric perovskites was developed by Kinase et al.[27] It is based on the model of a rigid lattice of ions, whose polarizabilities depend on their relative and absolute distances. Hence, in contrast with band theoretical descriptions[17,20] neither spectral nor temperature dependences can be predicted. However, at fixed light wavelength and temperature the physical origins of the observed RI changes are easily translated from one theory into the other. According to Kinase et al.[27] the P-optical properties originate from (i) the change of the dipole interaction and (ii) the change of the electronic polarizabilities, both being due to the lattice deformation, (iii) the spontaneous Kerr effect inducing a change of the electronic polarizabilities due to the local field.

The mechanisms (i) and (ii) are considered to represent the elasto-optical contribution to the RI's. The dipole interaction (i) involves a correction of the local Lorentz field. Calculations for $PbTiO_3$ (Ref. 29) predict $\delta n_c(i) = +0.10$ and $\delta n_a(i) = -0.01$, in sharp disagreement with our experimental values (at T_c) $\delta n_c = -0.11$ and $\delta n_a = -0.09$ An important correction driving both RI's negative can be expected from the mechanism (ii). Since the polarizability of an ion decreases with increasing overlap with its neighbors, there will be noticeable effects due to overlap between Ti and O in the [100] direction and between Pb and O in the (100) plane, respectively. For symmetry reasons the Ti-O overlap is responsible for δn_c,

whereas the Pb-O overlap will govern the behavior of δn_a. Since both types of overlap increase considerably in the polar state of $PbTiO_3$,[25] both n_a and n_c will decrease appreciably. Owing to the strong interaction of the $6s^2$ electrons of Pb^{2+} and four of the neighboring O^{2-} ions[25] the n_a shift must be quite strong. A quantitative estimate will be given below. It explains why n_a finally approaches n_c leaving only a comparatively small LB value. Since the increase of overlap is less important between Ba^{2+} and O^{2-} in $BaTiO_3$, n_a remains distant from n_c (Ref. 28) in that case and the LB becomes relatively large.

The local-field mechanism (iii), which may be considered as the clamped electro-optical effect, was quantitatively treated in the case of $BaTiO_3$.[27] It was shown to essentially drive the extraordinary RI, n_c, negative. A similar or even larger effect can be expected for $PbTiO_3$ owing to its large P_s values. A rough estimate following the calculations for $BaTiO_3$ (Ref. 27) may be given by $\delta n_c(\text{iii}) = -0.10$ and $\delta n_a(\text{iii}) = 0$. Hence, comparing $\delta n_j(i) + \delta n_j(\text{iii})$, $j = a$ and c, respectively, with the experimental data we are now able to estimate $\delta n_j(\text{ii})$, which escaped theoretical calculations up to now:[27] $\delta n_c(\text{ii}) = -0.11$ and $\delta n_a(\text{ii}) = -0.08$. These values appear reasonable in proportion to one another in view of the above discussion.

It is interesting to note that according to our estimate the elasto-optical contributions to δn_c, (i) and (ii), seem to cancel, whereas δn_a is virtually of elasto-optical origin. Thus conjecturing the proportionalities $\delta n_a \propto c/a - 1$ and $\delta n_c \propto P_s^2$ the slight nonproportionality of δn_a and δn_c would not be surprising, if $c/a - 1$ and P_s^2 were significantly nonproportional. Their common plot in Fig. 7, however, reveals nearly perfect proportionality. Slight differences arise only around 500–650 K, where P_s^2 rises somewhat less steeply than $c/a - 1$. This might account for some of the flattening of δn_c with respect to δn_a in that temperature range. A closer look, however, at the two sets of curves in Fig. 7 immediately indicates the far greater importance of higher-order terms contributing to the RI anomalies.[21] Tentatively being due to P_s^4 and $(c/a - 1)^2$, respectively, they are partially canceling the first-order contributions in accordance with theory in the case of the Kerr effect.[27] Moreover, it must be assumed that both corrections are different in weight thus explaining that δn_c saturates more rapidly than δn_a at low temperatures. This seems to be reminiscent of Känzig's[14] idea of a saturation of the internal field effect, which, however, must be extended by the idea of an independently saturating elasto-optical effect.

The foregoing discussion shows that, again, no simple explanation of the LB anomaly in $PbTiO_3$ seems to be possible. In particular, we have to abandon the simple separation of linear elasto- and quadratic electro-optical contributions to the RI anomalies in the spirit of the former attempt[11] used to explain the LB. Fits of our data of δn_a and δn_c to P_s^2 and $(c/a - 1)$, respectively, using relations corresponding to Eq. (2), totally failed and yielded no reasonable elasto- and polarization-optical coupling constants (i.e., really constant between 300 K and T_c). Obviously the previous success of this method[11] was fortuitous, based on very crude estimates of P_s (Ref. 22) and a much too flat LB curve. However, our present analysis

shows that the peculiar shape of the LB curve must not be taken too seriously. It simply emerges as a result of a small difference of two large quantities, which vary slightly differently with temperature. This, on the other hand, seems to be due to the different physical mechanisms involved. Further theoretical work is required for an explanation of these details, including the marked wavelength dependence of the Δn_{ac} versus T curve.[20]

ACKNOWLEDGMENTS

[1]G. Shirane and S. Hoshino, J. Phys. Soc. Jpn. **6**, 265 (1951).

[2]M. E. Lines and A. M. Glass, *Principles and Applications of Ferroelectrics and Related Materials* (Clarendon, Oxford, 1977), p. 248.

[3]G. Burns and B. A. Scott, Phys. Rev. Lett. **25**, 167 (1970).

[4]G. Shirane, J. D. Axe, J. Harada, and J. Remeika, Phys. Rev. B **2**, 155 (1970).

[5]K. A. Müller, in *Dynamical Critical Phenomena and Related Topics*, Vol. 104 of *Lecture Notes in Physics*, edited by C. P. Enz (Springer, Berlin, 1979), p. 210.

[6]R. Hofmann, S. H. Wemple, and H. Gränicher, J. Phys. Soc. Jpn. Suppl. **28**, 265 (1970); G. Burns and F. H. Dacol, Ferroelectrics **37**, 661 (1981).

[7]G. Burns, F. H. Dacol, J. P. Remeika, and W. Taylor, Phys. Rev. B **26**, 2707 (1982).

[8]W. Kleemann, F. J. Schäfer, and M. D. Fontana, Phys. Rev. B **30**, 1148 (1984).

[9]F. J. Schäfer and W. Kleemann, J. Appl. Phys. **57**, 2607 (1985).

[10]G. Shirane, R. Pepinsky, and B. C. Frazer, Acta Crystallogr. **9**, 131 (1956).

[11]S. A. Mabud and A. M. Glazer, J. Appl. Crystallogr. **12**, 49 (1979).

[12]J. Kobayashi, Y. Uesu, Y. Sakemi, and T. Hosokawa, Phys. Status Solidi A **59**, K143 (1980).

[13]J. Kobayashi, Y. Uesu, and Y. Sakemi, Phys. Rev. B **28**, 3866 (1983).

[14]W. Känzig (private communication), as quoted in Ref. 10.

[15]Yu. N. Venevtsev, G. S. Zhdanov, S. P. Solov'ev, and V. V. Ivanova, Sov. Phys.—Crystallogr. **4**, 235 (1959) [Kristallografiya **4**, 255 (1959)].

[16]A. M. Glazer and S. A. Mabud, Acta Crystallogr. B **34**, 1065 (1978).

[17]M. DiDomenico and S. H. Wemple, J. Appl. Phys. **40**, 720 (1969).

[18]P. D. Thacher, J. Appl. Phys. **41**, 4790 (1970).

[19]S. Singh, J. P. Remeika, and J. R. Potopowicz, Appl. Phys. Lett. **20**, 135 (1972).

[20]N. N. Kristofel and A. V. Gulbis, Opt. Spectrosc. (USSR) **49**, 175 (1980).

[21]J. Fousek and J. Petzelt, Phys. Status Solidi A **55**, 11 (1979).

[22]J. P. Remeika and A. M. Glass, Mater. Res. Bull. **5**, 37 (1970).

[23]W. N. Lawless, Phys. Rev. **138**, A1751 (1965).

[24]F. Pockels, *Lehrbuch der Kristalloptik* (Teubner, Leipzig, 1906).

[25]J. G. Bergman, G. R. Crane, and E. H. Turner, J. Solid State Chem. **21**, 127 (1977).

[26]E. P. Ippen, IEEE Quantum Electron. **2**, 152 (1966).

[27]W. Kinase, N. Ohnishi, M. Yoshikawa, and K. Mori, Ferroelectrics **56**, 165 (1984), and references therein.

[28]W. N. Lawless and R. C. de Vries, J. Appl. Phys. **35**, 2638 (1964).

[29]W. Kinase, J. Kobayashi, and N. Yamada, Phys. Rev. **116**, 348 (1959).