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Temperature Variations of Optical Indicatrix and Birefringence in Ferroelectric CsH_2PO_4

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The principal values and the rotation angle of the optical indcatrix and the optical birefringence of CsH_2PO_4 have been measured at 589 nm as a function of temperature both in the paraelectric and the ferroelectric phases. The principal values are found to be $n_\alpha=1.509$, $n_\beta=1.515$ and $n_\gamma=1.533$ at room temperature, where n_α is the value parallel to the *b*-axis. Rotation of the optical indicatrix with temperature about the *b*-axis is within 1° between 100 K and 300 K. The spontaneous birefringence determined for (010) plate by the usual procedure reaches a maximum at about 15 K below T_c, then becomes negative with decreasing temperature. Similar behavior is found for (100) plate. It is found that these anomalous behaviors of the spontaneous birefringence are caused by the similar anomalous behavior in the spontaneous strain through the elastooptic coupling.

§1. Introduction

Cesium dihydrogen phosphate, CsH_2PO_4, undergoes a ferroelectric phase transition at about 150 K.[1] The crystal is monoclinic with the space group $P2_1/m$ in the paraelectric phase.[2] Below the transition temperature, T_c, the spontaneous polarization takes place along the *b*-axis and the space group changes to $P2_1$.[2,3] According to the crystal structure analysis, hydrogen bonds in which protons are in spatially disorder in the paraelectric phase align along the *b*-axis.[4,5]

Recent neutron scattering studies[6] of CsH_2PO_4 have shown that a one-dimensional correlation between the polarization fluctuation dominates in a wide temperature range of the paraelectric phase. Owing to this point, extensive studies of CsH_2PO_4 are made by many investigators. Static dielectric constant in the paraelectric phase[7-9] shows pronounced deviation from the Curie-Weiss law in contrast with the most of the other ferroelectrics. This peculier behavior is interpreted by a quasi-one-dimensional Ising model,[10-12] though there remains some quantitative inconsistency between the theory and the experiment.[9] Recently, Uesu *et al.*[13] have reported that the electrostrictive constant derived from the spontaneous strain is different from that from the electric field induced strain. From this, they claimed that CsH_2PO_4 was an improper ferroelectric.

In the framework of the usual phenomenological theroy,[14] it is expected that the spontaneous strain and the spontaneous birefringence are proportional to the square of the spontaneous polarization in proper ferroelectrics having a center of symmetry in the paraelectric phase. It is worthwhile to investigate, therefore, the spontaneous changes of these quantities in order to clarify the behavior of the order parameter for the ferroelectric phase transition. In the case of the monoclinic system, two principal axes of an ellipsoid of the second rank tensor do not generally coincide with the crystallographic axes and change their directions with temperature. Therefore, there is little investigation on the relation between the order parameter and the spontaneous birefringence or the spontaneous strain in the monoclinic system as yet. The first aim of this paper is to determine the optical parameters of the monoclinic ferroelectric as a function of temperature.

A recent optical study of $PbHPO_4$[15] which is considered as a quasi-one-dimensional ferro-

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electric has shown that the spontaneous birefringence measured for the (010) plate is proportional to the square of spontaneous polarization in the temperature range $0.8 < T/T_c < 1$ as expected by the usual phenomenological theory. Uesu *et al.*[13] reported that the spontaneous strain of CsH_2PO_4 near T_c along the *b*-axis is proportional to the square of spontaneous polarization in the vicinity of the Curie temperature. These results imply that, in the quasi-one-dimensional ferroelectrics, the spontaneous strain as well as the spontaneous birefringence is explained in the framework of the usual phenomenological theory, though dielectric properties does not obey the usual phenomenological theory. Deguchi *et al.*[16,17] measured the spontaneous polarization and spontaneous strain of CsH_2PO_4 in a wide temperature range. They showed, in contradiction to the previous result,[13] that the spontaneous strain changes their sign at about 40 K below T_c whereas the spontaneous polarization does not exhibit any anomaly in the temperature range measured. Furthermore, as shown in the preceding paper,[18] the spontaneous birefringence of CsH_2PO_4 measured for (100) plate shows the anomaly very similar to that of the spontaneous strain.[16,17] The second aim of this paper is to clarify the anomalous behavior of the sontaneous birefringence of CsH_2PO_4 in connection with the ferroelectric phase transition.

In §2, experimental procedures are briefly stated. Experimentally obtained results are indicated in §3. The results are compared with the phenomenological theory and discussed in connection with the phase transition in CsH_2PO_4 in §4.

§2. Experimental

The compound CsH_2PO_4 was prepared by a reaction, $Cs_2CO_3 + 2H_3PO_4 \rightarrow 2CsH_2PO_4 + H_2O + CO_2$, in distilled water, using reagents of special grace. The single crystals were grown by slow cooling from aqueous solutions in the temperature range from about 40°C to 50°C after recrystallization. The NaD line (λ= 589 nm) was used in the measurements of the optical parameters stated below. Refractive indices were measured by a spectrometer using the method of minimum deviation.[19] Two kinds of prisms were cut out from the single crystals using a wet thread saw. The surface of the prisms were carefully polished with wet filter paper and a planed board. Relations between the light pass and the prism surfaces are indicated schematically in Fig. 1. In the prism a in which the *b*-axis lies on the bisecting

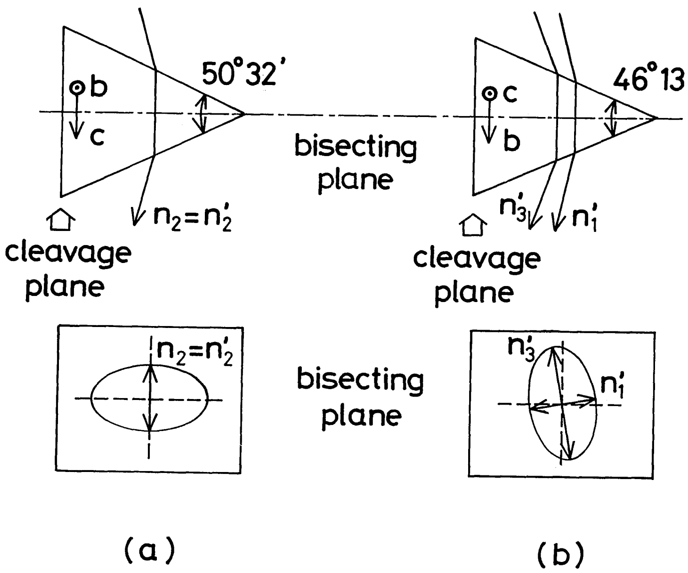

Fig. 1. Schematic representation of prism geometry in the condition of minimum deviation. Arrows in the bisecting planes indicate the direction of the electric displacement vectors of rays.

plane of the apex angle, the wave normal of light is parallel to the c-axis and perpendicular to the b-axis in the condition of minimum deviation. Then, we can get one of the principal refractive indices in which the electric displacement vector is parallel to the b-axis. In the prism b which has the bisecting plane of the apex angle perpendicular to the b-axis, the wave normal is parallel to the b-axis is the condition of minimum deviation. In this case, the condition of minimum deviation is fulfilled for light with the electric displacement vector parallel to one of the two principal axes of the optical indicatrix. Using these two prisms, all principal refractive indices can be obtained. The prisms were set in a cryostat mounted on the turn table of the spectrometer. The temperature of the prisms was controlled by thermal conduction from liquid nitrogen vessel through copper rods with a heater coil. Correction for dilatation of the specimen by temperature change was made by measuring the temperature dependence of the apex angle of the prisms. The transition temperature T_c was determined by the simultaneous measurement of dielectric constant ε_b.

The optical birefringence was measured by a Berek compensator with specimens of pillar shapes, $2\times 2\ \mathrm{mm}^2$ in area and 4 to 8 mm in length. The wave normal of light was parallel to the longest edges of these specimens. In the following birefringences for light with the wave normal parallel to the b- and c-axes are denoted by Δn_b and Δn_c, respectively, and that parallel to the a^*-axis which is taken to be perpendicular to both of the b- and c-axes is denoted as Δn_{a^*}. A cryostat with a liquid nitrogen container and a copper sample holder was used to control the temperature of the specimens. Correction for dilatation of the specimen was made by using the unit cell parameters measured by an X-ray four circle diffractometer. The transition temperature T_c was determined by simultaneous measurement of dielectric constant ε_b.

In order to determine the rotation angle of the optical indicatrix, a thin (010) plate was used. Orientation of the a-axis in the plate was determined by X-ray diffraction. Using a polarizing microscope with crossed nicols, an extinction position was determined by detecting the transmitted light intensity with CdS cell. The orientation of the optical indicatrix was obtained from the angle between the extinction position and the c-axis which is parallel to the edge of the cleavage plane.

§3. Results

3.1 Temperature dependence of the optical parameters

The orientation of the optical indicatrix in CsH_2PO_4 is illustrated exaggeratedly in Fig. 2.

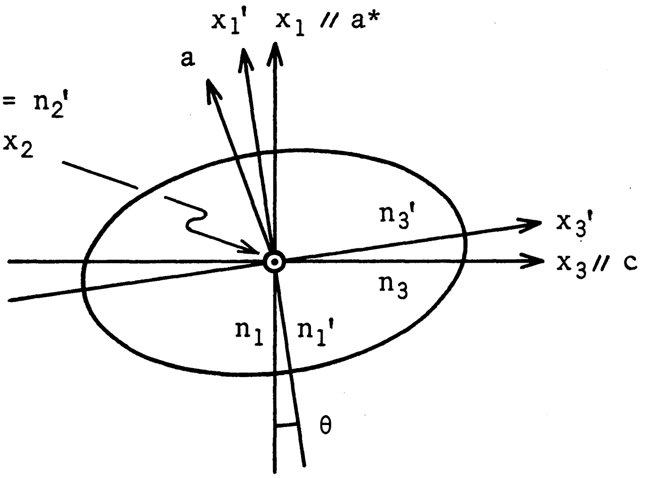

Fig. 2. Orientation of the indicatrix in CsH_2PO_4 crystal (exaggerated). Two Cartesian coordinate systems (x_1, x_2, x_3) and (x_1', x_2', x_3') are taken, respectively, in accordance with the crystallographic axial system and the principal axes of the indicatrix.

As seen in the figure, two principal axes lie in the *a–c* plane. We take two Cartesian coordinate systems (x_1', x_2', x_3') and (x_1, x_2, x_3). The coordinate axes x_1', x_2' and x_3' are taken in accordance with the principal axes of the indicatrix. The principal values of the indicatrix n_1', n_2', n_3' are the refractive indices for light propagating along the primed coordinate axes. On the other hand, the unprimed coordinate axes x_1, x_2 and x_3 are taken parallel to *a**-, *b*- and *c*-axes, respectively. The refractive indices represented by unprimed n_1, n_2 ($=n_2'$) and n_3 are those for light with the wave normal parallel to the unprimed coordinate axes as indicated in Fig. 2. The relation between the refractive indices of primed and unprimed systems is explained with relative dielectric impermeabilities.[20] The relation in the monoclinic crystal is described in Appendix.

The birefringences Δn_b, Δn_c and Δn_{a*} are related to the refractive indices as, $\Delta n_b = n_3' - n_1'$, $\Delta n_c = n_1 - n_2$ and $\Delta n_{a*} = n_3 - n_2$, respectively. The angle θ in Fig. 2 indicates the angle between the primed and the unprimed coordinates in the *a-c* plane, which varies with the rotation of indicatrix around the *b*-axis.

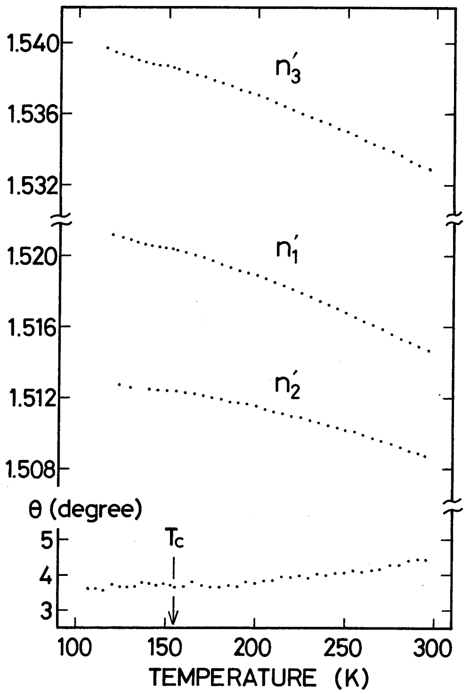

Fig. 3. Principal values and rotation angle of the optical indicatrix as a function of temperature.

Figure 3 shows the observed values of the principal refractive indices n_i' and the rotation angle of the optical indicatrix θ of CsH_2PO_4 as a function of temperature. In the paraelectric phase, all refractive indices show slight deviation from linear dependence with respect to temperature. The refractive indices n_1' and n_3' show very similar temperature dependence. Below T_c, all of the principal refractive indices exhibit slight deviations from the extrapolated values from high temperature region, but the order of these deviations is not so large compared to the precision of the spectrometer (1×10^{-4}). Rotation of the optical indicatrix represented by change in θ is within 1° in the temperature range from 100 K to 300 K and no appreciable change is detected at T_c. In the usual notation of the principal values of the optical indicatrix, n_α, n_β and n_γ ($n_\alpha < n_\beta < n_\gamma$), the room temperature values are $n_\alpha = n_2' = 1.508_7$, $n_\beta = n_1' = 1.514_7$ and $n_\gamma = n_3' = 1.532_9$. The angle V between the x_3' axis and an optical axis at room temperature was obtained to be 30.16° from the relation,

$$V = \tan^{-1}\sqrt{\frac{n_3'^2(n_1'^2 - n_2'^2)}{n_2'^2(n_3'^2 - n_1'^2)}}. \tag{1}$$

Then the crystal is optically positive.

Temperature dependence of the birefringence determined directly by the Berek compensator is shown in Fig. 4. The values of Δn_{a*} and Δn_c

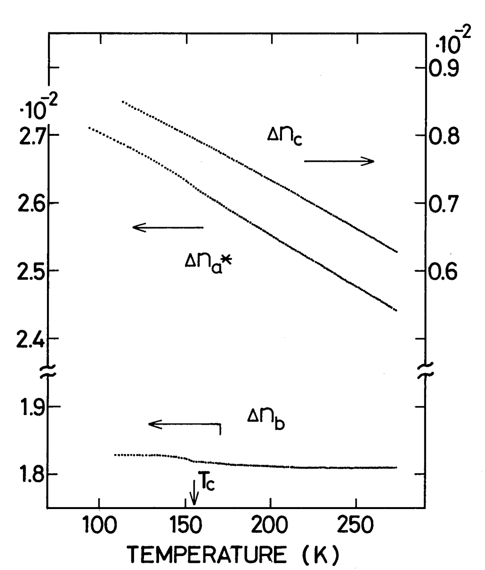

Fig. 4. Temperature dependence of birefringence.

decrease almost linearly with temperature, whereas Δn_b changes only slightly. Temperature dependences of Δn_b, Δn_{a*} and Δn_c were found to be consistent with the results of n'_i and θ obtained independently.

The change in the optical axial angle $2V$ with temperature can be calculated from the principal values of the optical indicatrix, n'_1, n'_2 and n'_3, indicated in Fig. 3 using eq. (1). However, it is more suitable to use the values of birefringence with one of the principal values, say n'_3, for the sake of small experimental errors. The optical axial angle $2V$ is expressed as,

$$2V=2\tan^{-1}\left\{\frac{\left[\left[\frac{1-\cos 2\theta}{2(n'_3-\Delta n_b)^2}+\frac{1+\cos 2\theta}{2n'^2_3}\right]^{-1/2}-\Delta n_{a*}\right]^{-2}-\frac{1}{(n'_3-\Delta n_b)^2}}{\frac{1}{(n'_3-\Delta n_b)^2}-\frac{1}{n'^2_3}}\right\}^{1/2}. \quad (2)$$

The values of $2V$ obtained from eq. (2) using the data in Figs. 3 and 4 are shown in Fig. 5. A slight deviation from the value extrapolated from the paraelectric phase is found below T_c.

3.2 Change in the optical parameters with the phase transition

The optical parameters of the crystal vary in response to changes in temperature and strain through the thermooptic and the elastooptic effects, respectively. The thermooptic and elastooptic coefficients are usually constants or slowly varying functions of temperature. Therefore, the relative dielectric impermeability a'_{ij} of the primed coordinate in Fig. 2 in the paraelectric phase can be expanded in terms of changes in temperature and strain,[14] ΔT and ΔS_{kl}, respectively, as

$$(a'_{ij})_{\text{para}}=a'^0_{ij}+\zeta_{ij}\Delta T+p_{ijkl}\Delta S_{kl}$$
$$=a'^0_{ij}+(\zeta_{ij}+p_{ijkl}\alpha_{kl})\Delta T. \quad (3)$$

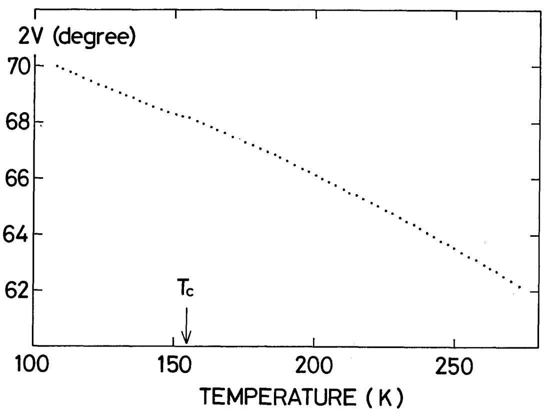

Fig. 5. Temperature dependence of optical axial angle $2V$ calculated from observed values of n'_3, θ, Δn_{a*} and Δn_b.

Here, a'^0_{ij} is the relative dielectric impermeability at a standard temperature, ζ_{ij} the thermooptic coefficient, p_{ijkl} the elastooptic coefficient and α_{kl} the thermal expansion coefficient.

In the ferroelectric phase, the optical parameters are altered by the onset of the spontaneous polarization. In the absence of the external electric field and mechanical stress, a'_{ij} can be represented as,

$$(a'_{ij})_{\text{ferro}}=a'^0_{ij}+(\zeta_{ij}+p_{ijkl}\alpha_{kl})\Delta T+p_{ijkl}\Delta S^s_{kl}, \quad (4)$$

where ΔS^s_{kl} is the component of the spontaneous strain. The first and the second terms on the right hand side have a meaning of the normal part of a'_{ij} which is supposed to exhibit no anomaly around the transition temperature. The spontaneous change of the relative dielectric impermeability $\Delta a'_{ij}$ in the ferroelectric phase corresponds to the third term on the right hand side as,

$$\Delta a'_{ij}=p_{ijkl}\Delta S^s_{kl}. \quad (5)$$

The spontaneous changes of n'_i are proportional to $\Delta a'_{ij}$ for small spontaneous changes from eq. (A·2) in Appendix. Unfortunately, the spontaneous changes of n'_i of CsH_2PO_4 are within 10^{-4} in order of magnitude as shown in Fig. 3, which are small among those of the ferroelectrics reported. These changes could not be determined with sufficient accuracy in the present experiment. Then, it is difficult to give quantitative consideration on the elastooptic effect associated with the phase transition from the data of refractive indices shown in Fig. 3.

In the paraelectric phase, the birefringence changes monotonically except in the vicinity of T_c as shown in Fig. 4. Then, the birefringence

Table I. Fitting parameters for birefringence in the paraelectric phase.
$\Delta n = a + bT + cT^2$ (6)

	a (10^{-2})	b $(10^{-5})[K^{-1}]$	c $(10^{-9})[K^{-2}]$
Δn_{a*}	2.8724(5)	−1.671(4)	3.5(1)
Δn_b	1.8756(5)	−0.534(5)	10.7(1)
Δn_c	0.9932(4)	−1.202(3)	−4.96(8)

Δn at temperature T in the paraelectric phase can be well approximated by an empirical formula,

$$\Delta n = a + bT + cT^2, \tag{6}$$

where a, b and c are constants independent of temperature. The birefringence Δn is the difference between the refractive indices of rays with electric displacement vectors parallel to the principal axes of the ellipse determined by the cross-section of the indicatrix perpendicular to the wave normal of the rays. Therefore, we assume that eq. (6) is a difference between the normal parts of refractive indices which are the inverse of the square root of a'_{ij} in eq. (3) or a_{ii} of the unprimed coordinate in Fig. 2 in the similar equation. The determined contants in eq. (6) for three birefringences shown in Fig. 4 are listed in Table I. In the ferroelectric phase, the birefringences deviated from eq. (6). Differences $\delta(\Delta n)$ between the observed values of Δn and those calculated by eq. (6) are shown in Fig. 6. The values of $\delta(\Delta n_{a*})$ and $\delta(\Delta n_b)$ exhibit maxima at about 15 K below T_c and change their signs at about 40 K below T_c. These behaviors can not be understood within the framework of the usual phenomenological theory, because $\delta(\Delta n)$ has the meaning of the spontaneous birefringence which is proportional to the square of the spontaneous polarization in the theory.

§4. Discussion

In order to clarify the cause of the anomalies found in $\delta(\Delta n)$, we investigate firstly the elastooptic effect due to spontaneous strain below T_c. Recently, Deguchi *et al.*[16,17] have reported thermal expansion of CsH_2PO_4 and showed that the spontaneous strain exhibits anomalous behavior like the spontaneous birefringences $\delta(\Delta n_{a*})$ and $\delta(\Delta n_b)$ shown in Fig. 6. Therefore, it is worth to examine

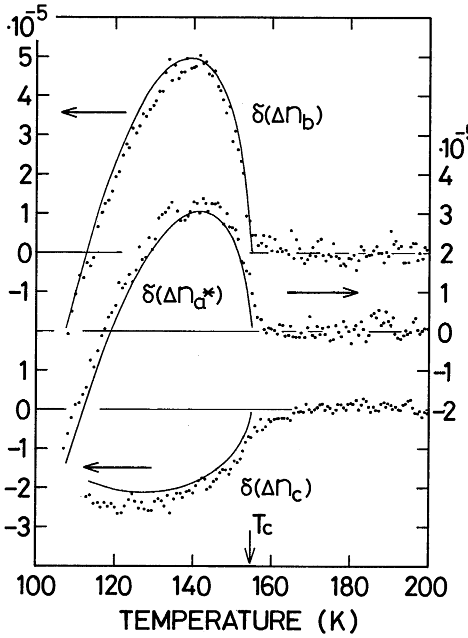

Fig. 6. Temperature dependence of the anomalous part of birefringence. Dots indicate the difference between the observed value of Δn and that calculated by eq. (6). Solid curves indicate the elastooptic contribution calculated by the use of eq. (7) with the experimentally obtained spontaneous strain.[17]

whether the temperature dependence of the spontaneous birefringence is consistent with the behavior of the spontaneous strain or not.

Using eqs. (A·2) and (A·3) in Appendix and eqs. (4) and (5) we obtain formulae for the spontaneous birefringence,

$$\left.\begin{aligned} &\delta(\Delta n_{a*}) = \frac{1}{2}(n_2^3 p_{22kl} - n_3^3 p_{33kl})\Delta S_{kl}^s, \\ &\delta(\Delta n_b) = (c_1 p_{11kl} + c_2 p_{33kl})\Delta S_{kl}^s, \\ &\text{and} \\ &\delta(\Delta n_c) = \frac{1}{2}(n_2^3 p_{22kl} - n_1^3 p_{11kl})\Delta S_{kl}^s, \end{aligned}\right\} \tag{7}$$

where c_1 and c_2 stand for

$$c_1 = \frac{1}{4}\left\{n_1'^3\left(1 + \frac{1}{\cos 2\theta}\right) - n_3'^3\left(1 - \frac{1}{\cos 2\theta}\right)\right\},$$

and

$$c_2 = \frac{1}{4}\left\{n_1'^3\left(1 - \frac{1}{\cos 2\theta}\right) - n_3'^3\left(1 + \frac{1}{\cos 2\theta}\right)\right\}.$$

Since the refractive indices n_i and n'_i and angle θ are slowly varying functions of temperature, we regard these quantities as constants and

Table II. Constants for elstooptic coupling effect in eq. (7).

kl	$\delta(\Delta n_{a*})$ $\frac{1}{2}(n_2^3 p_{22kl}-n_3^3 p_{33kl})$	$\delta(\Delta n_b)$ $c_1 p_{11kl}+c_2 p_{33kl}$	$\delta(\Delta n_c)$ $\frac{1}{2}(n_2^3 p_{22kl}-n_1^3 p_{11kl})$
11	0.490(65)	0.581(64)	−0.086(42)
22	−0.174(54)	−0.223(53)	0.047(35)
33	0.082(29)	0.174(28)	−0.091(19)
13	0.044(16)	0.059(16)	−0.015(11)

adopt the values at 154 K. Under these assumptions we determined coefficients of the elastooptic effect in eq. (7) by a least squares fit using the experimentally obtained spontaneous strains.[17] The values thus obtained are listed in Table II. Three spontaneous birefringences calculated by the use of eq. (7) with the values in Table II are described in Fig. 6 as the solid curves which well agree with the experimental values. This means that anomalous behavior of the spontaneous birefringence in CsH_2PO_4 is caused by the anomalous behavior of the spontaneous strain. Accordingly, the deviation of birefringence from eq. (6) in the ferroelectric phase can not be explained only by a direct contribution from P_s^2 through the electrooptic effect. If we assume an electrostrictive coupling of the form $\Delta S_{kl}^s = Q_{kl22}P_2^2$, anomalous temperature dependences of the spontaneous birefringences $\delta(\Delta n_b)$ and $\delta(\Delta n_{a*})$ shown in Fig. 6 require changes of the sign of the electrostrictive coefficients Q_{kl22}. However, direct observation of the electrostrictive coefficients through lattice distortion by application of external electric field shows no such change of sign of Q_{kl22} in the temperature range from T_c to 90 K.[17]

Similar anomalous behavior of the spontaneous birefringence as well as the spontaneous strain has been reported for $Ca_2Sr(C_2H_5CO_2)_6$.[21-23] Explanation of this behavior was made on the basis of the theory of the improper ferroelectrics[24] or the equivalent two sublattice model.[25] In the case of CsH_2PO_4, however, applicability of the equivalent two sublattice model is ruled out; for there is no pseudo-structure which yields above T_c the equivalent two sublattices in the structure below T_c.[3] In the theory of the improper ferroelectrics, a coupling between strain and a hidden order parameter together with the spontaneous polarization is taken into account. Anomaly in the hidden order parameter can cause the anomalous temperature dependence of the spontaneous strain. However, the Curie constant of CsH_2PO_4 in the paraelectric phase is of the order of 10^5 K which is much larger than the other known improper ferroelectrics. This large value of the Curie constant implies that the electric polarization is the order parameter for the ferroelectric phase transition in CsH_2PO_4. Furthermore, dielectric dispersion of CsH_2PO_4 is well described by a mono-dispersive relaxation[26] which contradicts to an expectation of the polydispersive nature in the dielectric relaxation of the improper ferroelectrics.[27] It must be necessary, therefore, to seek other possibility of the origin of the anomalous behavior in the framework of the proper ferroelectrics.

It is known that the dielectric constant of CsH_2PO_4 deviates appreciably from the Curie-Weiss law in a wide temperature range. This deviation is well explained by the theory of the quasi-one-dimensional ferroelectrics.[7,9] This model contains an excess entropy due to intrachain interaction in the paraelectric phase as well as in the ferroelectric phase in contrast with the usual phenomenological theory. Recent studies on the specific heat of CsH_2PO_4 have revealed that deviation of the specific heat from the normal part starts far apart from T_c, several tens or a hundred degrees from T_c in the paraelectric phase.[28,29] This means that the quasi-one-dimensional nature is found in a wide temperature region in CsH_2PO_4. Very recently, Nakamura *et al.*[30] have found that the excess entropy due to intrachain interaction in the quasi-one-dimensional Ising model gives an anomalous thermal strain even in the paraelectric phase. Then, the deviation from the normal part of the lattice strain in CsH_2PO_4 is expected to be different from that of the usual phenomenological theory. These facts imply, therefore, that the anomalous behavior of the spontaneous birefringence shown in Fig. 6 as well as that of the spontaneous strain[16,17] in CsH_2PO_4 are apparent one resulting from inadequacy of supposed normal parts, *e. g.* eq. (6). It is necessary to determine the anomalous part in the paraelectric phase along the line of the pseudo-one-dimensional model.

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Appendix

For the primed and unprimed systems in Fig. 2, the optical indicatrix of the monoclinic crystal is represented by using the relative dielectric impermeability[20] a'_{ij} and a_{ij} as,

$$\left.\begin{aligned} &a'_{11}x'^2_1+a'_{22}x'^2_2+a'_{33}x'^2_3=1,\\ &a_{11}x^2_1+a_{22}x^2_2+a_{33}x^2_3+2a_{13}x_1x_3=1,\\ &\text{with}\\ &a_{13}=\frac{1}{2}(a_{33}-a_{11})\tan 2\theta. \end{aligned}\right\} \quad (\mathrm{A}\cdot 1)$$

Here, dielectric impermeability a_{ii} and a'_{ii} and the refractive indices n_i and n'_i are related, respectively, as

$$a_{ii}=\left(\frac{1}{n_i}\right)^2 \quad \text{and} \quad a'_{ii}=\left(\frac{1}{n'_i}\right)^2. \quad (\mathrm{A}\cdot 2)$$

It is found that there are following relations between the components of a'_{ij} and a_{ij},

$$\left.\begin{aligned} &a'_{11}=\frac{1}{2}a_{11}\left(1+\frac{1}{\cos 2\theta}\right)+\frac{1}{2}a_{33}\left(1-\frac{1}{\cos 2\theta}\right),\\ &a'_{22}=a_{22},\\ &a'_{33}=\frac{1}{2}a_{11}\left(1-\frac{1}{\cos 2\theta}\right)+\frac{1}{2}a_{33}\left(1+\frac{1}{\cos 2\theta}\right). \end{aligned}\right\} \quad (\mathrm{A}\cdot 3)$$

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