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Optical study of $LiKSO_4$ crystals under uniaxial pressure

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An optical study of $LiKSO_4$ crystals under uniaxial pressure is presented. The evolution of the birefringence Δn_{ab} and Δn_{bc} has been measured in the temperature range 100–300 K. A ferroelastic monodomain has been induced in the biaxial low-temperature phase by means of uniaxial pressure applied perpendicular to the c axis. The dependence of the birefringence Δn_{ab} with respect to the applied uniaxial pressure σ_{yy} has been measured and related to the piezo-optic coefficients π_{ij}. Our conclusions seem to conciliate the discrepancies presented in previous optical studies of $LiKSO_4$ crystals.

I. INTRODUCTION

Lithium potassium sulfate is a singular compound of the A_2BX_4 family due to its unusual sequence of phase transitions (PT's). It has been exhaustively investigated in recent years by means of different experimental techniques.[1–11] However, there still remain open a number of basic questions related to the existence of some phase transitions and the symmetry of some phases. There are three major reasons for the controversies found in the literature: (i) a complicated pattern of twinnings in the whole temperature range; (ii) ferroelastic domains at low temperature; and (iii) the coexistence of different structures in some temperature ranges.

In this paper we will focus our attention on the temperature range 100–300 K. Two phase transitions occur in this interval: at about 205 and 185 K when the crystal is cooled. In the heating process, these phase transitions are shifted to 250 and 190 K, respectively. We will use in this paper the notation adopted in a number of previous articles which is schematically summarized below.

V		IV		III
	$T_{F^+}=190$ K ↑		$T_{\Delta^+}=250$ K ↑	
	$T_{F^-}=185$ K ↓		$T_{\Delta^-}=205$ K ↓	

The structure of the room-temperature phase (III) of $LiKSO_4$ (LKS) has been known since 1925.[12] It belongs to the C_6^6 ($P6_3$) space group with two formulas per unit cell. The structures of phases IV and V were the object of controversies in the past; some authors proposed a hexagonal symmetry to phase IV and an orthorhombic symmetry to phase V,[2] while others supported trigonal and monoclinic structures for phases IV and V, respectively.[3,5] It is well accepted today that phase IV belongs to the trigonal space group C_{3v}^4 ($P31c$),[13] and there is strong experimental evidence showing that phase V has monoclinic symmetry.[5,6,11] Recently, the importance of considering the symmetry laws relating the twin domains, which generate a macroscopic symmetry greater than the symmetry of a single domain, was demonstrated.[11]

Another important aspect of phase V is the existence of ferroelastic domains below 190 K.[1,7] It has been shown that a ferroelastic monodomain can be induced with ordinary uniaxial pressure (100 bar) applied parallel to the b axis.[11]

In this paper we present the results and analysis of an optical study of crystalline $LiKSO_4$ under uniaxial pressure between 100 and 300 K. Measurements of the temperature dependence of both in-plane (Δn_{ab}) and out-of-plane birefringence (Δn_{bc}) in phase V are presented. These measurements were only possible due to the induction of a ferroelastic monodomain in this phase by applying uniaxial pressure σ_{yy} along the b axis. Moreover, a systematic study of the dependence of Δn_{ab} on the uniaxial pressure σ_{yy} was carried out and is also presented. This study allows the determination of the piezo-optical effect of LKS in the experimental configuration used.

The principal aim of this study is to clarify the discrepancies concerning the symmetry of phase IV pointed out in the previous optical studies on crystals reported in the literature[4,6] and to measure the spontaneous birefringence Δn_{ab} in a ferroelastic monodomain of phase V. On the other hand, it is shown that the uniaxial pressure breaks the axial symmetry of phases III and IV, giving rise to the apparent biaxial character observed previously.[4]

II. EXPERIMENTAL DETAILS

$LiKSO_4$ single crystals were grown from aqueous solution by slow evaporation at $T=40\,°C$. The samples used in these experiments were cut from untwinned regions, which had high optical quality. Samples of about 4–10 mm^3 were carefully polished in order to be strain-free. The crystallographic axis was determined by x-ray diffraction. The c axis is the hexagonal axis and the a axis is perpendicular to c, and parallel to a natural face of the crystal. The birefringence was measured using the Sènarmont method, with a computer-controlled apparatus having a mechanical resolution which allows the measurement of a phase difference of about 0.01°. This accuracy corresponds typically to an ultimate resolution of $\delta(\Delta n) \le 3\times10^{-8}$. The mechanical pressure was measured using a home-made calibrated stress-gauge system, having a resolution of $\delta p = \pm 0.5$ bar and reproducibility of 1%. The stress-gauge system was adapted to a gas-flow cryostat, allowing the study of the uniaxial pressure dependence of Δn at low temperature, down to $T=10$ K. It is important to remark that all measurements were per-

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formed after a temperature stabilization better than 0.1 K. Moreover, great care was taken in order to prevent the coexistence of different phases; so the phase transitions were crossed at rates lower than 1 K/min.

III. RESULTS

The temperature dependence of the *bc*-plane birefringence of LKS is shown in Fig. 1, displayed as $\Delta n_{bc}(T)-\Delta n_{bc}(300\text{ K})$. These measurements were carried out under a constant uniaxial pressure $\sigma_{yy}=50$ bar applied along the *b* axis. These data were taken according to the following procedures. First of all, a small temperature cycle was carried out around the phase boundary of the III-IV PT. The sample was cooled down to 190 K. At this temperature, the cycle was reversed and the birefringence was measured on heating (see open squares in Fig. 1). After that a large temperature cycle was carried out, by cooling the sample through the IV-V phase boundary down to 80 K. The data taken on cooling (open circles) and in the heating process (full circles) following this last procedure are displayed in Fig. 1.

Our results in the small temperature cycle are in good agreement with previous results.[4,6] Owing to the extremely slow dynamics of the reconstructive III-IV PT, the phase boundaries depend strongly on the cooling and heating rates and on the applied uniaxial pressure, as well as on the history of the sample. It turns out to be almost impossible to observe exactly the same critical temperatures in different runs.

Very surprisingly, we have observed an excess of Δn_{bc} in phase IV in the heating process after the large temperature cycle within the range $T>190$ K. Thus, the signal of the small temperature cycle is not recovered after crossing the IV-V PT. This can be established by comparing the heating curves in the small (open squares) and large temperature cycle (full circles) in Fig. 1. One could naively expect such a tail behavior above the IV-V phase boundary as a natural consequence of applying a symmetry-breaking stress field. However, the *irreversible character* of the observed feature is not yet understood. It seems that some finite clusters of the ferroelastic phase still remain in the trigonal phase in the large temperature cycle procedure. The mechanism of the pinning forces involved here should be the aim of future investigations.

By continuing the cooling process, the IV-V PT is observed at about 177 K (see Fig. 1). In spite of the applied uniaxial pressure ($\sigma_{yy}=50$ bar), the sample still remains very inhomogeneous due to domain structures which persist until temperatures far below the PT. On that account, the behavior of the birefringence curve is in general not reproducible. Moreover, the application of a smaller uniaxial pressure changes the behavior of this curve completely. This is exemplified in the inset to Fig. 1, where, in the cooling process under $\sigma_{yy}=15$ bar (open triangles in the inset), Δn_{bc} decreases and increases once more in an arbitrary way.

In the heating process, a shift of the critical temperatures to higher values with increasing uniaxial pressure can be observed. This can be seen, for example, by comparing the heating curves in Fig. 1 (full circles, $T_{F^+}\approx 182$ K under $\sigma_{yy}=50$ bar) with that in the inset (full triangles, $T_{F^+}\approx 177$ K under $\sigma_{yy}=15$ bar).

Figure 2 shows the temperature dependence of the in-plane birefringence Δn_{ab} of LKS under constant uniaxial pressure, $\sigma_{yy}=20$ bar. Several jumps in the birefringence signal in the temperature range 75–185 K are observed during the cooling process (see open circles in Fig. 2). These jumps occur at distinct temperatures in different samples or different regions in the same sample. Once more, the samples are in general extremely inhomogeneous in this temperature range. On crossing the sample the laser beam is strongly diffracted, showing a characteristic diffraction pattern with sixfold symmetry. All these effects can be ascribed to the coexistence of different ferroelastic domains as already reported.[6] Below $T\approx 75$ K, the temperature dependence of Δn_{ab}

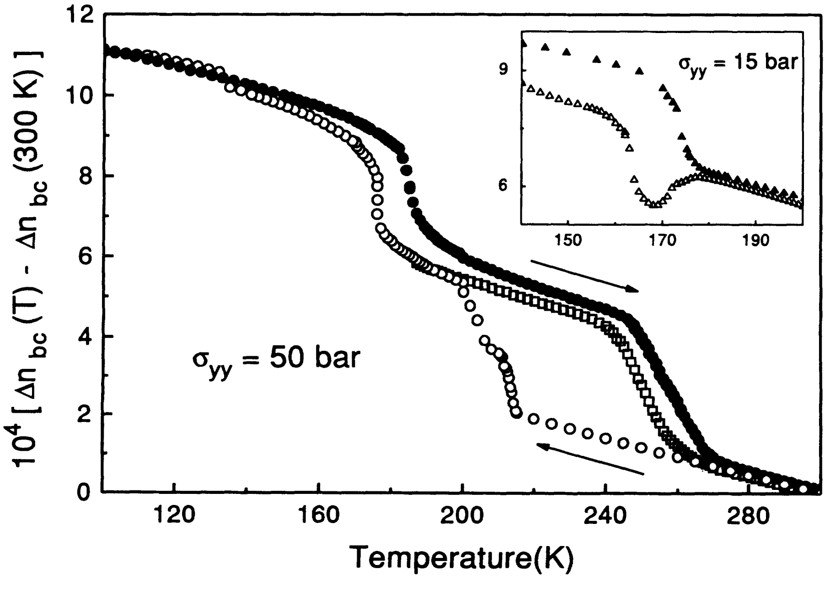

FIG. 1. Temperature dependence of the out-of-plane birefringence of $LiKSO_4$, $\Delta n_{bc}(T)-\Delta n_{bc}(300\text{ K})$, under constant uniaxial pressure ($\sigma_{yy}=50$ bar), in the cooling (open circles) and heating (full circles) process, after the large temperature cycle, the temperature being reversed at 80 K. Open squares show the heating curves after the small temperature cycle, reversing temperature 190 K. The inset shows the cooling (open triangles) and the heating curves (full triangles) under $\sigma_{yy}=15$ bar.

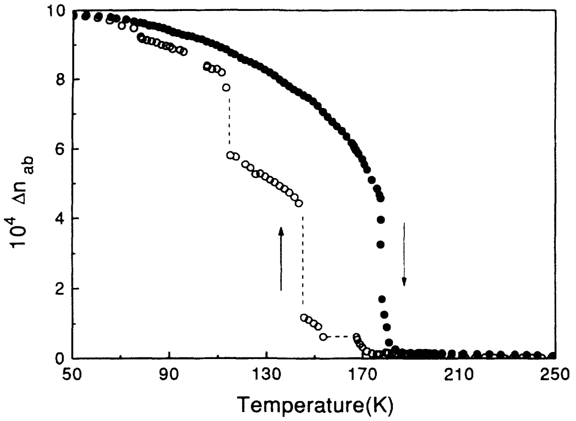

FIG. 2. Temperature dependence of the in-plane birefringence of $LiKSO_4$, $\Delta n_{ab}(T)$, under constant uniaxial pressure ($\sigma_{yy}=20$ bar) in the cooling (open circles) and heating (full circles) process. Dashed lines are guides for the eyes.

varies smoothly, indicating that the sample has achieved a monodomain state. This is confirmed by the disappearance of the sixfold-symmetry diffraction pattern.

During the heating process, the sample shows a characteristic signal of a monodomain, with an amplitude of about $\Delta n_{\max}=10^{-3}$ at 50 K, which decreases with increasing temperature and vanishes at the critical temperature $T_{\Delta^+}=180\pm1$ K (see full circles in Fig. 2). It must be emphasized that this value of the birefringence in the *ab* plane was not observed in previous optical studies of LKS,[4,6] due to the lack of control of the ferroelastic domains in those experiments.

As shown in Fig. 3, a very small but measurable birefringence signal Δn_{ab} of about 10^{-5} was observed in phase IV, when the crystal was submitted to a uniaxial pressure of $\sigma_{yy}=20$ bar. This fact is rather surprising, owing to the expected uniaxial character of the trigonal symmetry proposed for this phase.[13] A signal of the same order of magnitude has also been observed by Ivanov,[4] but not by Kleemann, Schäfer, and Chaves.[6] However, no birefringence signal $\Delta n_{ab}(T)$ was observed in phase IV, when the measurement was done without applied pressure (see stars in Fig. 3). The results of Ref. 6 are therefore reproduced.

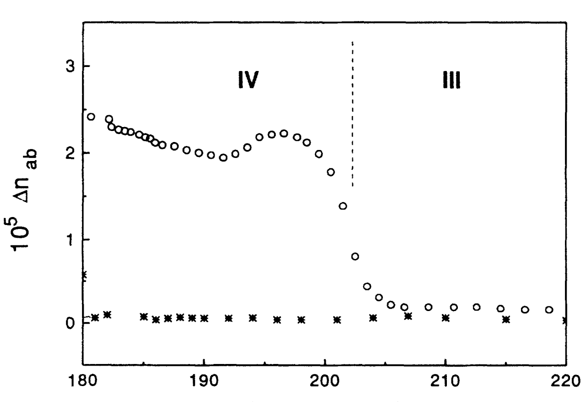

FIG. 3. Temperature dependence of the in-plane birefringence of $LiKSO_4$, $\Delta n_{ab}(T)$, in the vicinity of the III-IV PT, without uniaxial pressure (stars) and under constant uniaxial pressure ($\sigma_{yy}=20$ bar, open circles). Measurements were carried out on cooling.

In order to clarify this contradiction, a systematic study of the dependence of the birefringence Δn_{ab} with respect to the applied uniaxial pressure σ_{yy} was carried out. Typical results are shown in Fig. 4. All these measurements were recorded on increasing applied pressure. For each curve, the temperature was first increased in order to eliminate a monodomain structure and then decreased to the next temperature without applied pressure. Only after this procedure was the pressure applied.

Within phase III the behavior of Δn_{ab} vs σ_{yy} is observed to be linear and practically temperature independent. All the curves in this case fall together, as can be seen in Fig. 4(a) for $T=300$ K (full diamonds), 250 K (open down triangles), and 230 K (stars). On cooling the crystal, the gradual appearance of phase IV manifests itself by the increase of the slope in these curves, as shown

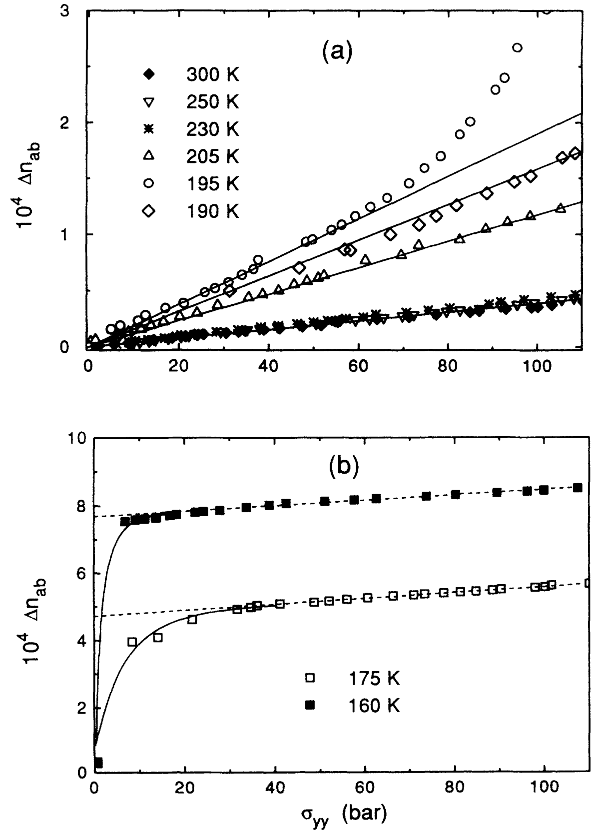

FIG. 4. Δn_{ab} vs σ_{yy} for different temperatures in (a) phases III and IV: $T=300$ K (full diamonds), 250 K (open down triangles), 230 K (stars), 205 K (open up triangles), 195 K (open circles), and 190 K (open diamonds); and in (b) phase V: 175 K (open squares) and 160 K (full squares). Dashed lines are the best fits in the linear regions (see text) and full lines are guides for the eyes.

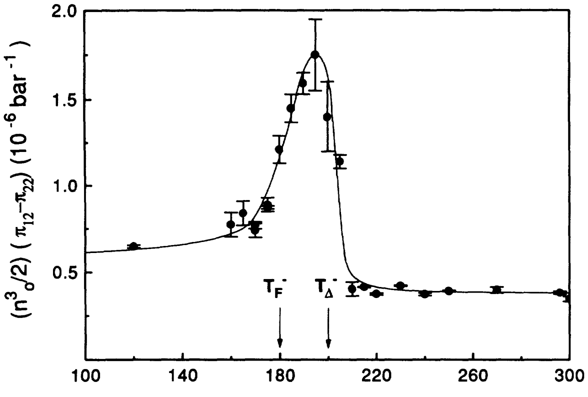

FIG. 5. Temperature dependence of the piezo-optical coefficient $(n_0^3/2)(\pi_{12}-\pi_{22})$, obtained by the fitting of some curves like those shown in Fig. 4 (see text). The sample was prepared by cooling without applied uniaxial pressure.

for example for $T=205$ K (open up triangles) and $T=195$ K (open circles). By continuing the cooling process we observe a decrease in the slope, indicating the proximity of the ferroelastic PT [see $T=190$ K, open diamonds, in Fig. 4(a)]. In both phases III and IV the extrapolation of these straight lines to $\sigma_{yy}=0$ bar indicates no spontaneous birefringence in the *ab* plane. Furthermore, the slopes of these curves are related to the piezo-optical coefficients π_{ij}. These results allow us to conclude that a small uniaxial pressure σ_{yy} applied in phases III and IV gives rise to a birefringence signal Δn_{ab} due to the piezo-optical effect.

Figure 4(b) shows that the behavior of the Δn_{ab} vs σ_{yy} curves in phase V contrasts sharply with the dependence found in phases III and IV (see curves for $T=175$ and 160 K, represented by open and full squares, respectively). A nonlinear behavior can be observed for the low-pressure region ($\sigma_{yy}\leq 40$ bar for $T=175$ K). This effect is undoubtedly related to the reorientation of ferroelastic domains, which will be recalled in more detail in the next section. For now, let us only point out that the linear behavior found at higher pressure is ascribed to the monodomain dependence of Δn_{ab} vs σ_{yy} in the ferroelastic phase V. The extrapolation of these straight lines to $\sigma_{yy}=0$ bar gives the real value of spontaneous Δn_{ab}.

Considering the experimental configuration, it can be easily demonstrated that the slope of the fitting curves corresponds to $(n_0^3/2)(\pi_{12}-\pi_{22})$ in all phases (see the Appendix), whose temperature dependence is depicted in Fig. 5. The determination of these parameters in phase IV is less precise than in phases III and V. Therefore, we use the error bars, which indicate the range of the physically acceptable fits. The phase transitions are clearly observed as discontinuities in the temperature behavior of these piezo-optical coefficients. Due to the fact that these data were taken after the cooling procedure, only the critical temperatures T_{Δ^-} and T_{F^-} are assigned.

IV. DISCUSSION

In the last section it was shown that our results concerning the in-plane and out-of-plane birefringence of LKS in the room-temperature phase III are in complete accordance with the previous optical studies. However, this is not true for phases IV and V. Let us discuss these two phases separately.

Phase IV. As already mentioned in the Introduction, a birefringence signal has been observed in the *ab* plane by Ivanov.[4] This result led Ivanov to conclude that this phase should have a symmetry lower than trigonal. On the other hand, Kleemann, Schäfer, and Chaves[6] did not observe a measurable birefringence in this plane, thus supporting the trigonal symmetry proposed by several authors. We have shown in Fig. 3 that a small uniaxial pressure applied perpendicular to the *c* axis is enough to generate a measurable Δn_{ab} signal in phase IV. Thus, we are able to reproduce both results, depending on the application of a uniaxial pressure on the sample. The origin of this signal is the difference in the piezo-optical coefficients of the hexagonal and the trigonal phases, which is clearly shown in Fig. 5. Note that the presence of a constant applied uniaxial pressure cannot be evidenced by the temperature dependence of Δn_{ab} in the room-temperature phase since the effective piezo-optical coefficients in this phase are virtually temperature independent. We conclude that, very probably, the manner that Ivanov[4] used to fix the sample into the cryostat generated a stress in the sample and, consequently, a residual birefringence signal in the *ab* plane. Our results confirm the uniaxial symmetry for phase IV.

An increase of the slope in the Δn_{ab} vs σ_{yy} curve for $\sigma_{yy}>80$ bar has been observed close to the IV-V phase transition [$T=195$ K, open circles in Fig. 4(a)]. This behavior is not yet well understood. Probably it is related to the effect of the uniaxial pressure on the critical temperature. As already pointed out, the uniaxial pressure shifts this PT to higher values of temperature. In order to clarify this feature, the determination of the σ_{yy} vs T phase diagram should be interesting.

Phase V. In this phase, our results concerning the birefringence in the *ab* plane are absolutely different from those previously reported. Kleemann, Schäfer, and Chaves[6] observed no measurable signal of Δn_{ab} below 190 K, whereas Ivanov[4] observed a small signal of about 5×10^{-6}. In our experiments, a birefringence signal of $\Delta n_{ab}\approx 10^{-3}$ has been observed at $T=100$ K.

Indeed, a very small ($\Delta n_{ab}\leq 2\times10^{-6}$) and not reproducible birefringence signal was observed if no pressure had been applied to the sample. Furthermore, by applying an extremely small uniaxial pressure ($\sigma_{yy}\leq 10$ bar) we observed a jump in the signal. This nonlinear behavior, which occurs in the beginning of the Δn_{ab} vs σ_{yy} curves [see open and full squares in Fig. 4(b)], can be clearly ascribed to domain reorientation within the ferroelastic phase. The ferroelastic domains reorient themselves with increasing applied pressure and a ferroelastic monodomain dominates the whole sample when the uniaxial pressure is greater than a given value which depends on temperature [40 bar for $T=175$ K in Fig. 4(b)]. Thus, for higher values of uniaxial pressure, the Δn_{ab} vs σ_{yy} curves become linear, and this corresponds to the expected monodomain behavior. The reorientation of the ferroelastic domains is also responsible for the discontinuous jumps of the Δn_{ab} curve in the cooling process (open circles in Fig. 2). In this context, we can also understand the different behavior of the out-of-plane birefringence Δn_{bc} for different applied pressures (see Fig. 1 and its inset).

The three kinds of ferroelastic domains (and, thus, the principal axis of the indicatrix) are rotated with respect to each other by 120° around the *c* axis. Therefore, in a multidomain sample, the average birefringence in the *ab* plane is expected to be null or very small. This explains the results obtained previously for this phase.[4,6]

Finally, the importance of the determination of $\Delta n_{ab}(T)$ in the ferroelastic phase must be emphasized. It is expected to be proportional to the order parameter of the ferroelastic PT. This seems to have been confirmed very recently by a high-precision x-ray experiment.[14]

V. CONCLUSIONS

A complete optical study of $LiKSO_4$ crystals has been performed in the temperature range 100–300 K, under uniaxial pressure applied along the *b* axis. The importance of inducing a ferroelastic monodomain in order to measure the spontaneous birefringence in the *ab* plane has been stressed. It was also shown that the applied pressure breaks the axial symmetry of the refractive index tensors in phases III and IV through a piezo-optical effect, thus generating a birefringence in the *ab* plane. The dependence of the birefringence Δn_{ab} with respect to the applied uniaxial pressure σ_{yy} was presented for some temperatures in phases III, IV, and V. The results show that phase IV has axial symmetry, in accordance with several results in the literature. We have measured the monodomain birefringence Δn_{ab} in the ferroelastic phase, which is expected to be proportional to the order parameter of this PT. Our conclusions seem to reconcile the previous optical studies of $LiKSO_4$ crystals.

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APPENDIX

The anisotropy of the refractive index of a crystal can be specified by the indicatrix,[15] which is an ellipsoid,

$$B_{ij}x_ix_j=1 ,$$

whose coefficients B_{ij} are the components of the relative dielectric impermeability tensor

$$B_{ij}=\kappa_0\partial E_i/\partial D_j .$$

A small perturbation in the values of the refractive index due the application of a moderate stress σ_{kl} can be approximated linearly by

$$\Delta B_{ij}=\pi_{ijkl}\sigma_{kl} ,$$

where π_{ijkl} are the piezo-optical coefficients. Regarding the symmetry of the crystal, the number of independent coefficients[15] is limited to 8, 12, and 20 for the hexagonal (class 6), trigonal (class 3), and monoclinic symmetry classes, respectively. Taking a reference frame (x_1,x_2,x_3) parallel to the crystallographic axes (a,b,c), it can be shown that the perturbed indicatrix for these classes yields the following.

Hexagonal.

$$(B_0+\pi_{12}\sigma_2)x_1^2+(B_0+\pi_{11}\sigma_2)x_2^2 +(B_e+\pi_{31}\sigma_2)x_3^2+\pi_{61}\sigma_2x_1x_2=1 .$$

Trigonal.

$$(B_0+\pi_{12}\sigma_2)x_1^2+(B_0+\pi_{11}\sigma_2)x_2^2+(B_e+\pi_{31}\sigma_2)x_3^2 -\pi_{41}\sigma_2x_2x_3+\pi_{52}\sigma_2x_1x_3+\pi_{62}\sigma_2x_1x_2=1 .$$

Monoclinic.

$$(B_0+\pi_{12}\sigma_2)x_1^2+(B_0+\pi_{22}\sigma_2)x_2^2 +(B_e+\pi_{32}\sigma_2)x_3^2+\pi_{62}\sigma_2x_1x_2=1 .$$

Here we are using the Voigt notation, $\sigma_2=\sigma_{yy}$, $\pi_{61}=\pi_{xyxx}$, etc.

If the laser beam crosses the crystal propagating along the *c* axis (x_3), with the apparatus oriented parallel to the *a* and *b* axes in order to measure $\Delta n_{ab}(0°)$, we obtain the same result for all three phases:

$$\Delta n_{ab}(0°)=-\tfrac{1}{2}n_0^3(\pi_{22}-\pi_{12})\sigma_2 ,$$

since $\pi_{11}=\pi_{22}$ in both uniaxial phases. In the same way it can be shown that, by rotating the crystal by 45°, Δn_{ab} becomes

$$\Delta n_{ab}(45°)=-\tfrac{1}{2}n_0^3\pi_{62}\sigma_2$$

for all phases, since $|\pi_{61}|=|\pi_{62}|$ in the uniaxial phases. This last configuration was not used in this study, but should be of interest in order to confirm the monoclinic symmetry at low temperature, since that for an orthorhombic phase $\pi_{61}=\pi_{62}=0$.

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