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Simultaneous determination of the birefringence, optical activity and rotation of the indicatrix of triglicine sulphate

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Abstract. The birefringence, rotation of the optical indicatrix and optical activity of triglicine sulphate (TGS) have been measured in the paraelectric and ferroelectric phases using a high-accuracy universal polarimeter (HAUP). The present measurements are compared with results already published in the literature and, surprisingly, many of them have been found to be in clear disagreement. Possible sources of systematic error are pointed out in the case of the optical activity measurements. The spontaneous parts of the different optical properties in the ferroelectric phase have been studied. These parts can be considered to develop under the exclusive influence of the spontaneous polarization. Simple relationships between the spontaneous optical quantities and the spontaneous polarization (quadratic for birefringence and indicatrix angle, and linear for gyration) are observed. Several electro-optic and electrogyration coefficients referred to the polarization are evaluated.

1. Introduction

Triglicine sulphate, $(\text{NH}_2\text{CH}_2\text{CO}_2\text{H})_3\cdot\text{H}_2\text{SO}_4$, (abbreviated as TGS) is one of the crystals that has received a lot of attention throughout the history of ferroelectricity. However, some of its most important optical parameters, and in particular the anisotropy of the optical susceptibilities, have been determined with only relative success. This is in part due to the low symmetry of the crystal, which permits the simultaneous appearance of various physical quantities whose effects overlap. In the paraelectric phase (point group $2/m$) birefringence appears combined with rotation of the optical indicatrix about the twofold axis. In the ferroelectric phase (point group 2) the situation is even worse because optical activity is superimposed to these two effects.

The birefringence of TGS crystals has been studied since the late 1960s. Nevertheless, results that vary by about 15% for the absolute value of birefringence along the ferroelectric y axis Δn at room temperature have been reported in the literature [1-3] and even the sign of the birefringence induced by the phase transition (the spontaneous birefringence $\delta_s \Delta n$) is still a matter of controversy. Likewise, there exist serious discrepancies in the results found by several authors [2-4] for the temperature dependence of the rotation of the optical indicatrix θ about the y axis. On the other

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hand, although there have been several measurements of the optical activity along isotropic crystal sections (also with contradictory results) [5, 6], there is only one measurement published for the optical activity G along the y axis in the ferroelectric phase [3]. This measurement was performed using the so-called high-accuracy universal polarimeter (HAUP), and this is, in principle, the only measuring technique able to provide reliable information about the optical activity in birefringent sections. Nevertheless, since the time of this experiment, the HAUP system has been substantially improved [7–9] and some sources of systematic error in the original method [10] have been discovered and corrected. This has stimulated us to undertake further optical studies in TGS.

In this paper we report on the results of the application of the HAUP method to TGS, both in the paraelectric and ferroelectric phases. We will present measurements of Δn , θ and G as functions of temperature. Likewise, several electro-optic and electrogyration coefficients, referred to the polarization, will be presented. The measurements have been carried out using a HAUP device built in our laboratory.

2. Experimental details

TGS crystals were grown at 42 °C from an aqueous solution using a dynamic method [11]. Large crystals (up to 4 cm long) of very good optical quality with well developed faces were obtained. The sample was a plane parallel plate, 1.824 mm thick, obtained by cleavage along (010) planes. The surfaces were polished using diamond paste with a grain size of 1 μm . All the surface area, except for a small hole for light passage, was coated with evaporated gold. Prior to the measurement the sample was kept at 95 °C for 24 h and, afterwards, it was slowly cooled down to room temperature under an electric field of 2 kV cm^{-1} . This treatment guarantees a monodomain sample free of internal stress. Measurements were performed, heating in steps of 1 °C at null field.

The HAUP device has been described in detail elsewhere [12]. Figure 1 shows a block diagram of the apparatus. It is worthwhile to mention that no optical components are placed between the sample and polarizers, and the sample holder has no windows. This is very important because, as has been shown [12], even the small residual-strain birefringence of the windows can produce systematic errors which make the final results completely unreliable.

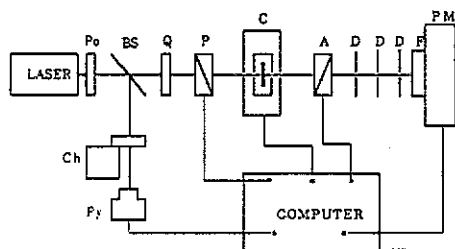


Figure 1. Block diagram of the HAUP equipment. Po, polaroid film; BS, beam splitter; Q, quarter-wave plate; P, polarizer; C, sample cryostat; A, analyser; D, diaphragm; F, interference filter; PM, photomultiplier; Ch, mechanical chopper; Py, pyroelectric detector.

The system of data collection and analysis is also explained in [12]. Briefly, for each temperature, the transmitted light intensity is measured as a function of Θ , the

angle between the polarizer and the sample fast axis, and Y , the relative polarizer-analyser angle. In order to avoid systematic errors in the subsequent refinement of data, it is important to use a (Θ, Y) region well centred around the absolute minimum of the transmitted intensity [13]. In our case, 11×11 (Θ, Y) positions were scanned in steps of 1.6×10^{-3} rad. The birefringence, optical activity and rotation of indicatrix were obtained from a global linear least-squares fit of all the experimental data following the procedure described in [9]. The so-called δY and γ errors were removed by adopting the method proposed in [7].

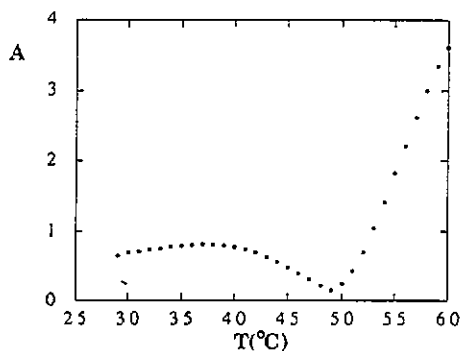


Figure 2. Temperature dependence of $A = 4 \sin^2 \Delta/2$.

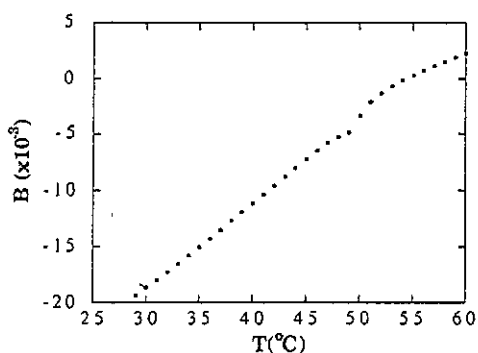


Figure 3. Temperature dependence of the quantity $B = -[(p + q)/2] \cot(\Delta/2) - \delta Y/2 + \theta$.

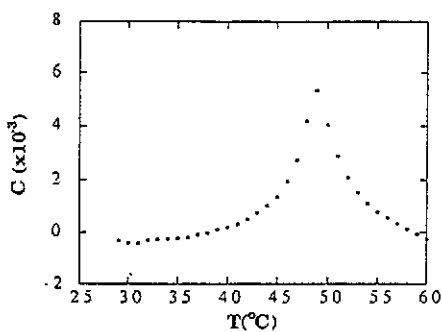


Figure 4. Temperature dependence of the quantity $C = -(2k - \gamma) + \delta Y \cot(\Delta/2)$.

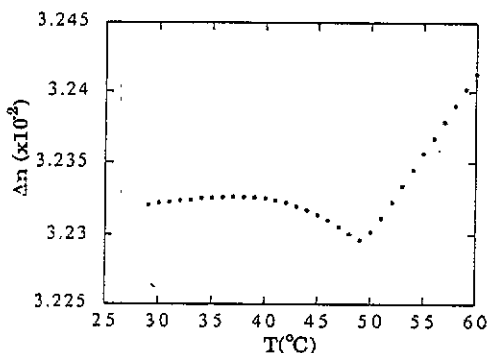


Figure 5. Temperature dependence of the birefringence of TGS along the ferroelectric axis.

3. Results and discussion

Figures 2, 3 and 4 show the temperature dependence of the quantities

$$A = 4 \sin^2(\Delta/2) \tag{1a}$$

$$B = -\frac{1}{2}(p + q) \cot(\Delta/2) - \frac{1}{2}\delta Y + \theta \tag{1b}$$

$$C = -(2k - \gamma) + \delta Y \cot(\Delta/2) \tag{1c}$$

which are the parameters directly determined from the raw data in the refinement process. Here p and q stand for the parasitic ellipticities of the polarizer and analyser, $\gamma = p - q$, δY is the deviation of the analyser angle from the crossed position, θ the indicatrix angle (except for a constant) and

$$\Delta = (2\pi/\lambda) \Delta n d \quad k = G/(2\bar{n}) \Delta n$$

where Δn , G and \bar{n} are the birefringence, optical activity and mean refractive index of the sample, d its thickness and λ the light wavelength in vacuum.

The birefringence derived from figure 2 is plotted in figure 5. In order to obtain the absolute value of Δn , the A data were supplemented with a measurement at room temperature of the optical retardation using a Berek compensator. The sign in the variation of Δ with temperature was checked by the same means. Thermal expansion corrections were not considered for the calculation of the Δn values. Considering the available thermal expansion data [14], these corrections should affect our results by less than 0.6% in the worst case.

As can be seen, $\delta_s \Delta n$ is positive, in disagreement with some results obtained with conventional methods [2] and with the HAUP device [3]. The absolute Δn also differs somewhat from the values reported in the referred works and, furthermore, the slope of Δn above the phase transition temperature T_c is completely different. Although Δn in [2] and [3] was measured at $\lambda = 529$ and 515 nm respectively, and we have used $\lambda = 633$ nm, it does not seem reasonable that this difference could affect the Δn behaviour too much. On the other hand, our data agree very well with the results reported by Kusto [15, 16]. Likewise, a quite similar temperature dependence of Δn has been found in related materials such as deuterated TGS, TGSe and deuterated TGSe [17]. It is difficult to explain such big discrepancies, especially those connected with the slope of Δn above T_c but, in view of them, we repeated the Δn measurements using different samples and a different measuring technique. The results remained the same. We conclude therefore that some systematic error was present in the measurements reported in [2] and [3].

The rotation of the optical indicatrix was deduced from the B data. In order to subtract the contributions of the parasitic ellipticities of the polarizers to B , a linear temperature dependence for θ above T_c was assumed. Under these conditions, the derivative of B with respect to the temperature T must be a linear function of $d(\cot \Delta/2)/dT$ since

$$dB/dT = -\frac{1}{2}(p+q)(d/dT)(\cot(\Delta/2)) + d\theta/dT. \quad (2)$$

Figure 6 shows that this is in fact our case. From the parameters of the fit we calculated $p+q = 1.71 \times 10^{-3}$ and $d\theta/dT = 2.53 \times 10^{-4}$ rad $^{\circ}\text{C}^{-1}$. Figure 7 gives the temperature dependence of the rotation of the optical indicatrix relative to its value at T_c . Our θ values are in good agreement with those reported by Kobayashi *et al* [3] although the slope above T_c is somewhat smaller in our case.

The optical activity was derived from the C values. As can be seen in figure 4, C presents a marked cotangent-like singularity around $T = 50^{\circ}\text{C}$. This anomaly does not take place entirely because of the phase transition but is mainly produced by the small A value at this temperature, which makes $\cot(\Delta/2)$ diverge. The spurious δY contribution, together with the γ error, were removed from a linear fit of C versus $\cot(\Delta/2)$ in the paraelectric phase, where k is known to be zero (see

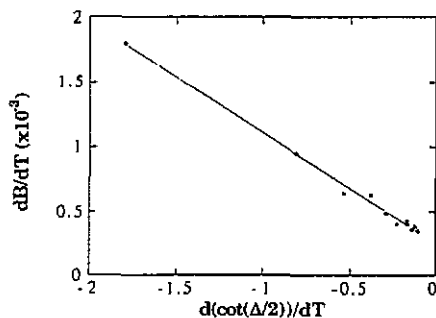


Figure 6. Relationship between dB/dT and $d(\cot \Delta/2)/dT$ in the paraelectric phase of TGS.

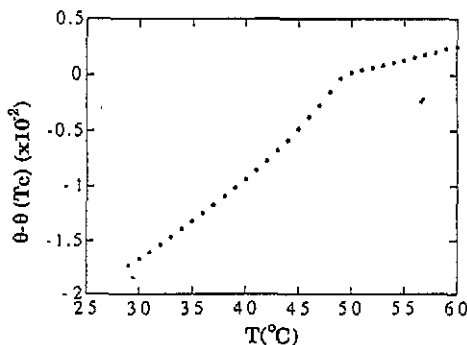


Figure 7. Temperature dependence of the indicatrix angle of TGS.

figure 8). The parameters γ and δY were determined to be $\gamma = -5.43 \times 10^{-4}$ and $\delta Y = 1.18 \times 10^{-3}$. The optical activity is represented in figure 9. An average refractive index $\bar{n} = 1.528$ independent of temperature was assumed. According to [1], corrections due to the change of \bar{n} with temperature would modify our results by less than 0.3%. As can be seen, optical activity points near T_c are of worse quality than the rest because the singularity is not fully suppressed. However, it is worth noticing that the accuracy obtained for G is rather good, presenting a noise much smaller than that considered usual in this kind of measurement. In comparison with the results of Kobayashi *et al* [3] (the only publication in which measurements of this quantity are given), our data are systematically higher by almost an order of magnitude. However, they would have to be smaller, since optical activity presents normal dispersion in the visible region [6]. This remarkable difference could arise because in [3] the δY contribution to the C data (later discovered by Kobayashi himself and coworkers [7, 8]) was not removed. As is evident from comparison of figures 4 and 9, the lack of consideration of the δY factor can produce large systematic errors in the determination of the optical activity.

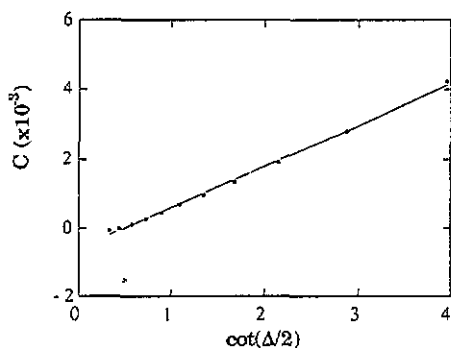


Figure 8. Relation of C with respect to $\cot(\Delta/2)$ in the paraelectric phase of TGS.

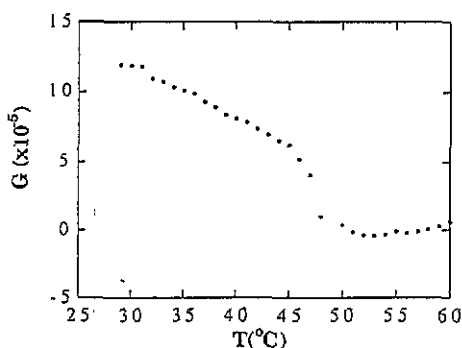


Figure 9. Temperature dependence of the optical activity along the ferroelectric axis of TGS.

We now turn to discuss the relationship between the spontaneous polarization in

the ferroelectric phase P_s and the contributions induced by the phase transition in the different optical properties.

Since the paraelectric phase is centrosymmetric, there are no linear electro-optic coefficients affecting the optical impermeability tensor B_{ij} . Electro-optic effects appear via a quadratic coupling with the spontaneous polarization. Therefore, if P_{si} are the components of the spontaneous polarization, we have

$$\delta_s B_{ij} = M_{ijkl} P_{sk} P_{sl} \quad (3)$$

where $\delta_s B_{ij}$ represents the spontaneous change of B_{ij} , and M_{ijkl} are the quadratic electro-optic coefficients. Likewise, the components of the gyration tensor in the ferroelectric phase g_{ij} can be written as

$$g_{ij} = \nu_{ijk} P_{sk} \quad (4)$$

in terms of the linear electrogyration coefficients ν_{ijk} .

Expressing (3) and (4) with reference to the principal axes of the paraelectric phase, we obtain the following equations for the relevant coefficients

$$\delta_s B_{ii} = M_{ii22} P_s^2 \quad (5a)$$

$$\delta_s B_{13} = M_{1322} P_s^2 \quad (5b)$$

$$g_{22} = \nu_{222} P_s. \quad (5c)$$

Denoting by B_i and B_i^0 the principal values of the impermeability tensor in the ferro and paraelectric phases, the spontaneous birefringence along the ferroelectric axis can be written, up to second-order in P_s , as

$$\delta_s \Delta n = B_1^{-1/2} - B_3^{-1/2} - (B_1^{0-1/2} - B_3^{0-1/2}) = M P_s^2 \quad (6)$$

where

$$M = \frac{1}{2} (M_{3322} B_3^{0-3/2} - M_{1122} B_1^{0-3/2}). \quad (7)$$

The spontaneous indicatrix angle $\delta_s \theta$ is expressed as

$$\tan 2\delta_s \theta = 2B_{13} / (B_{33} - B_{11}). \quad (8)$$

As $\delta_s \theta$ is small, $\tan 2\delta_s \theta \approx 2\delta_s \theta$ and, neglecting terms in P_s^4 , we obtain

$$\delta_s \theta = M' P_s^2 \quad (9)$$

where $M' = M_{1322} / (B_3^0 - B_1^0)$.

Finally, from 5(c) the optical activity along the ferroelectric axis takes the simple form

$$G = \nu_{222} P_s. \quad (10)$$

Figures 10, 11 and 12 show the relation between $\delta_s \Delta n$, $\delta_s \theta$ and G , and the spontaneous polarization. Polarization data were taken from Gonzalo [18]. In the cases

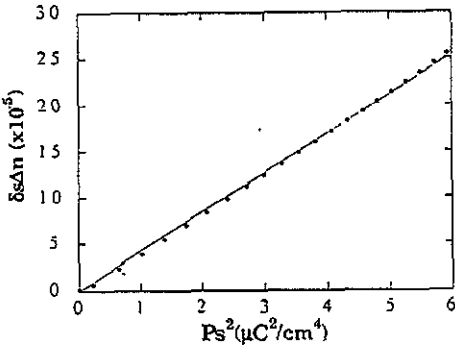


Figure 10. Relationship between the spontaneous birefringence and the spontaneous polarization of TGS.

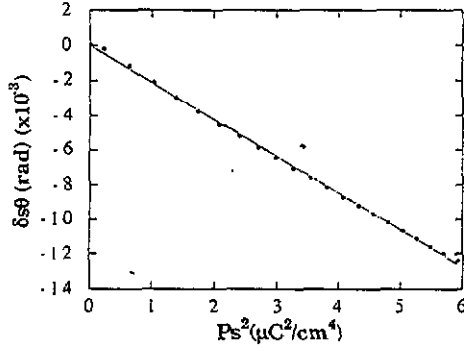


Figure 11. Relationship between the spontaneous part of the indicatrix angle and the spontaneous polarization of TGS.

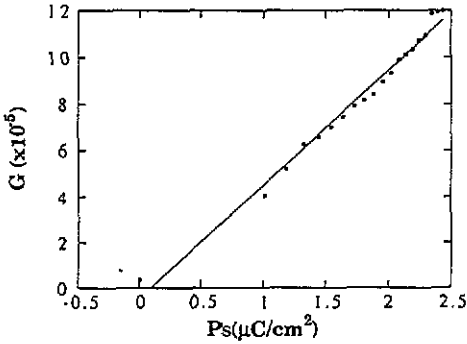


Figure 12. Relationship between the optical activity and the spontaneous polarization of TGS.

of Δn and θ , the normal contributions were taken to be linear extrapolations of the measured values at the paraelectric phase. The quadratic dependence of $\delta_s \Delta n$ and $\delta_s \theta$, and linear dependence of G can be clearly seen, in agreement with (6), (9) and (10). From the slopes of the three plots (figures 10, 11 and 12) we have determined $M = 0.424 \text{ m}^4 \text{ C}^{-2}$, $M' = -21.3 \text{ m}^4 \text{ C}^{-2}$ and $\nu_{222} = 5 \times 10^{-3} \text{ m}^2 \text{ C}^{-1}$.

We will finally evaluate the g_{11} coefficient from the values of $G = g_{22}$ and the optical activity along one of the optic axes given in [5]. In TGS the optical axes lie on the xy plane (where x and y refer to the principal directions of B_{ij}) and the gyration G' along them can be expressed as

$$G' = g_{11} \cos^2 V + g_{22} \sin^2 V \tag{11}$$

where $2V$ is the angle between the optical axes. V is practically temperature independent, $V = 30.8^\circ$ [1], so G' must be proportional to P_s , $G' = \nu' P_s$, as is experimentally observed [5, 6]. Therefore, the proportionality factor between g_{11} and P_s is given by

$$\nu_{112} = (\nu' - \nu_{222} \sin^2 V) / \cos^2 V. \tag{12}$$

We have calculated $\nu_{112} = -1.7 \times 10^{-3} \text{ m}^2 \text{ C}^{-1}$, which implies the existence of two directions on the xz plane along which the optical activity is zero. Curiously, these directions, at $\phi = \pm 30^\circ$ from the x axis, are almost coincident with the optical axes.

Acknowledgments

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