
Temperature Dependence of the Optical Activity of Pure and Deuterated Rochelle Salt Crystals

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Temperature dependence of the optical rotatory power (ρ) along the optical axis of pure and deuterated Rochelle salt single crystals has been given. Three phases of both crystals were examined and found to be optically active. The relation between spontaneous electrogyration (ρ_s) and spontaneous polarization (P_s) can be described by $\rho_s \propto P_s^2$. Moreover, the antipolar domains of pure and deuterated ferroelectric Rochelle salt crystals were found of the rotation twin-type not occurring in the enantiomorphic form, in contrast to those in other ferroelectric crystals, e.g., TGS-type and $\text{Pb}_5\text{Ge}_3\text{O}_{11}$.

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1. Introduction

Sodium potassium tartrate tetrahydrate ($\text{NaKC}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$), known as Rochelle salt (RS), has been the first ferroelectric material discovered [1]. The crystal structure of RS in two paraelectric phases, below $T_{c_1} = 255$ K and above $T_{c_2} = 297$ K, is orthorhombic (space group $P2_12_12$); in the intermediate ferroelectric phase it is monoclinic (space group $P2_1$) [2]. Deuterated Rochelle salt ($\text{NaKC}_4\text{H}_2\text{D}_2\text{O}_6 \cdot 4\text{D}_2\text{O}$ — DRS) is isostructural to RS but $T_{c_1} = 251$ K and $T_{c_2} = 308$ K [2].

Optical activity (OA) can occur in all three phases of RS and DRS crystals in agreement with their symmetry. The OA of RS crystal was found by Dufet [3] long before its ferroelectric properties were discovered. Optical rotatory dispersion (ORD) of RS was studied by Kozik [4] at room temperature. Further discussion of

the ORD and circular dichroism (CD) of the RS as well as DRS crystals at room temperature was reported by Koralewski and Mróz [5].

The first measurements of temperature dependence of OA along the optical axis of RS were performed by Levy [6] who related OA directly to the spontaneous polarization (P_s). However, these results were not confirmed by the later studies of Hermelbracht and Unruh [7], and Vlokh et al. [8]. Vlokh et al. [8] reported that for the electric field (E) greater than the coercive field (E_c) of RS the optical rotatory power (ρ) does not depend on the sign and the value of the external electric field. The same authors [8] proved that the shape of $\rho(E)$ dependence was close to the hysteresis loop of the butterfly-type, in contrast to the analogous dependence observed for TGS-type [9] and $\text{Pb}_5\text{Ge}_3\text{O}_{11}$ crystals [10]. A more detailed discussion of the $\rho(E)$ dependence for RS and TGS crystals was given by Kobayashi et al. [11]. These authors established experimentally that the antipolar domains in RS are not enantiomorphic and are united by hemitrope twin mechanism. The most recent measurements of Kobayashi et al. [12] showed that spontaneous gyration in the direction of the ferroelectric x -axis was proportional to P_s^2 . For the optical axis direction a similar relation may be expected, however, till now there is no experimental evidence.

The temperature dependence of DRS single crystal as well as the effect of deuteration on OA have not been discussed up to date, so these and the ambiguities in the hitherto reported temperature measurements and their interpretation have lead us to undertake a study of the temperature dependence of OA along the optical axis of RS single crystal as well as its deuterated analogue.

2. Experimental

Single crystals of RS were grown by slow evaporation of saturated aqueous solution at room temperature. Single crystals of DRS were grown according to the procedure described by Holden and Mason [13]. Both crystals of size of $\sim 20 \times 30 \times 50 \text{ mm}^3$ were colourless, transparent, and showed a good optical quality. The degree of deuteration (D) was estimated according to Holden and Mason [13] on the basis of the higher T_{c_2} and lower T_{c_1} Curie points, and found to be $D \approx 90\%$ and $D \approx 55\%$ for two different crystals. Crystals with higher ($T_{c_1} = 252 \text{ K}$ and $T_{c_2} = 306.8 \text{ K}$) and lower ($T_{c_1} = 253.7 \text{ K}$ and $T_{c_2} = 300.7 \text{ K}$) degree of deuteration will be labelled as DRS_I and DRS_{II} , respectively. The samples were prepared in the form of rods of 5–9 mm in diameter and 3–7 mm in length, with the axis parallel to one of the optical axes of the crystal. The direction of the optical axis was determined and controlled during the temperature measurements by means of the conoscopic method. The experimental set-up was the same as described previously [9, 14, 15]. The measurements were carried out using a He–Ne laser ($\lambda = 632.8 \text{ nm}$) as a light source.

3. Results and discussion

Measurements of the optical rotatory power of RS and DRS crystals in the ferroelectric phase have been made in the external electric field whose value was increased up to 200 kV/m, thus, much above the coercive field of these crystals ($E_c^{\text{RS}} \simeq 20$ kV/m, $E_c^{\text{DRS}} \simeq 40$ kV/m [2]), and whose sign was alternated. It was shown that the sign of ρ does not change and only the value of ρ changes slightly when the polarization is reversed. The changes could be described by a butterfly-type hysteresis loop. A typical relation $\rho(E)$ for the crystal DRS_{II} is shown in Fig. 1. The hysteresis loop observed for DRS is similar to the gyration

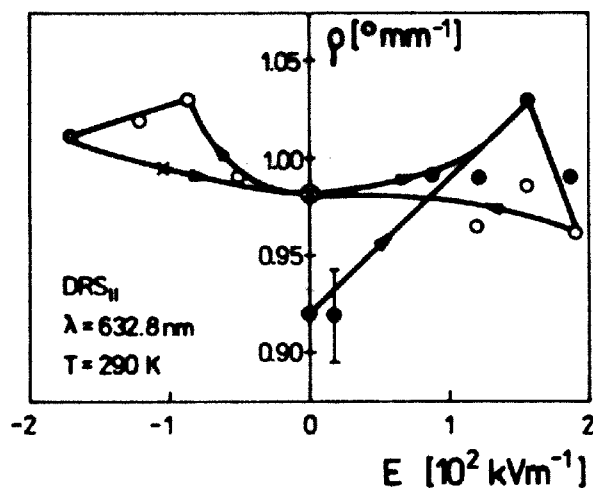


Fig. 1. The hysteresis loop of the optical rotatory power of DRS_{II} crystal at 290 K. The closed, open, and crossed points denote the direction (see also arrows) of the electric field changes.

loops reported by Vlokh et al. [8] and Kobayashi et al. [11] for pure RS crystals. Therefore, we can conclude that the domains in DRS are not enantiomorphic — similarly as in the RS crystals. This would mean that, according to the nomenclature of Shuvalov et al. [16, 17], the antipolar domains in RS and DRS crystals are of the rotatory twin-type. The asymmetric shape of the hysteresis loop observed by us and by other authors [8, 11] indicates a certain instability of the domain structure of RS and DRS crystals, which would at least partly explain a significant scatter of measuring points in the temperature and electric field dependences of ρ .

The optical rotatory power of RS and DRS crystals was measured in the temperature range of 245–315 K. For a few temperatures ρ was measured both at $E > E_c$ and at $E = 0$. The values obtained in these two series of measurements were comparable within the experimental error and were characterized by a similar scatter. Therefore, systematic measurements of ρ in the above temperature

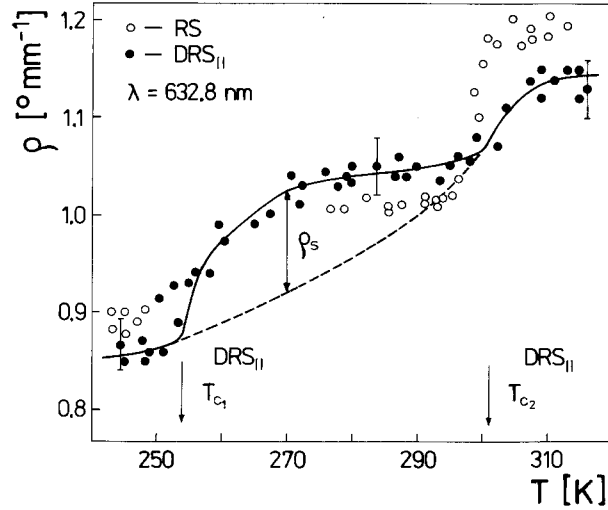


Fig. 2. The optical rotatory power ρ versus temperature for RS and DRS_{II} crystals, ρ_s is the spontaneous optical rotatory power.

range were carried out for $E = 0$ after a preliminary multiple polarization reversal of a given sample in the field $E > E_c$. The results are shown in Fig. 2. The observed changes of OA at the phase transition temperature T_{c2} are continuous (Fig. 2), which confirms the conclusions following from other data [2, 18] that the phase transition is continuous in both studied crystals. In spite of the fact that the temperature changes were very slow and at each temperature the sample was stabilized for about 2 hours before making a series of measurements, the results show a certain scatter of ρ values. This scatter and a significant uncertainty of measurements much exceeding the uncertainty of the measuring set-up is a consequence of the above-mentioned instability of the domain structure, high deliquescence of the crystals, and the process of their decomposition above a certain temperature. The rate of dehydration, that is the loss of crystalline water [19, 20], depends on temperature and pressure conditions. At 309 K the Rochelle salt decomposes into $\text{K}_2\text{C}_4\text{H}_4\text{O}_6 \cdot \frac{1}{2}\text{H}_2\text{O}$ and $\text{Na}_2\text{C}_4\text{H}_4\text{O}_6 \cdot 2\text{H}_2\text{O}$, while at 323.5 K these salts undergo the irreversible decay [19]. This process determines the upper limit of temperatures in the high-temperature paraelectric phase, in which the OA of RS and DRS crystals can be studied. The low-temperature limit was not so drastic, but below 273 K when the sample was under reduced pressure, in vacuum, the process of dehydration was faster. The occurrence of these processes was limited by all possible means, but a total elimination of their influence on the results of measurements of ρ was impossible.

The uncertainty of measurements and the scatter of the values of ρ for RS and DRS crystals are similar to those obtained by Hermelbracht and Unruh [7], and Vlokh et al. [8] for RS. Our values of ρ determined for RS are in very good

agreement with the results reported in [7, 8] for all the three phases but are contradictory to the results obtained by Levy [6] for the ferroelectric phase. The change $\Delta\rho$ in the range from $+18^\circ\text{C}$ to -18°C observed by Levy gave a symmetric bell-shaped curve with a maximum of -1.6°mm^{-1} at 0°C . The temperature dependence of $\Delta\rho$ Levy interpreted as related to the temperature changes of the spontaneous polarization. As we will show, his supposition about the correlation between $\Delta\rho$ and P_s is correct, but the absolute value of the $\Delta\rho$ changes and their sign are doubtful in a view of our results and those given in [7, 8].

The temperature changes of the optical rotatory power of DRS are similar to those observed for RS. In the paraelectric phase the optical rotatory power of DRS is smaller than that of RS while in the ferroelectric phase the reverse relation $\rho^{\text{DRS}} > \rho^{\text{RS}}$ is true (Fig. 2). The influence of deuteration on the optical rotatory power is illustrated in Fig. 3. The reverse relation in the ferroelectric phase can be

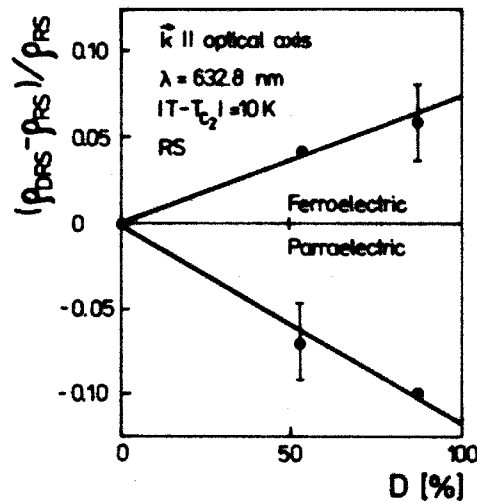


Fig. 3. Changes of the optical rotatory power of the RS crystals in the paraelectric phase at $(T - T_{c_2}) = 10$ K and in the ferroelectric phase at $(T_{c_2} - T) = 10$ K for different degrees of deuteration D .

a result of an increase (about 1.5 times) of P_s in the deuterated crystal (see [2]). The optical rotatory power of the ferroelectric phase cannot be related directly to the value of P_s , as suggested by Helmerbracht and Unruh [7]. The discussion of the relationship between OA and P_s requires an estimation of the spontaneous contribution to the total value of ρ in the ferroelectric phase. Because of a small range of experimentally available temperatures in the high-temperature paraelectric phase of RS and DRS, and rather large uncertainty of the ρ values, a separation (analytical or graphical) of the contribution related to the paraelectric phase is difficult and charged with a large uncertainty. Nevertheless, such a separation is the only

possibility of determination of the spontaneous optical activity along the optical axis. The $\rho_s(T)$ was determined as illustrated in Fig. 2. The spontaneous optical rotatory power was found graphically as the difference between the broken and solid lines representing the contribution of the paraelectric phase to OA and the total OA in the ferroelectric phase, respectively. The estimated values of ρ_s are small. For comparison with some other optically biaxial ferroelectric crystals they are collected in the Table. It is worth noting that the character of the temperature dependence of ρ in the paraelectric phase is more pronounced for the LAT [21] and NAT [22] crystals from the RS family, for which the ferroelectric transition points are better separated from their temperatures of decomposition.

TABLE

Spontaneous optical rotatory power ρ_s for some optically biaxial ferroelectric crystals ($\mathbf{k} \parallel$ optical axis, $\lambda = 632.8$ nm, $|T_c - T| = 20$ K).

Crystal	ρ_s [$^{\circ}\text{mm}^{-1}$]	Refs.
RS	0.06	
DRS	0.08	
LAT	0.62	[21]
TGS	0.17	[14, 15]
DTGS	0.23	[9, 15]
TGSe	0.49	[9]

The temperature variations of ρ reflect the temperature changes of the components of the g_{ij} tensor and the change of the angle $2V$ between the optical axes as well as the temperature changes of the light refractive index. The OA of RS and DRS crystals along the optical axis in the paraelectric phase can be described by the following relation:

$$\rho = \frac{\pi}{\lambda n_0} (g_{11} \cos^2 V + g_{33} \sin^2 V), \quad (1)$$

where n_0 denotes the light refractive index along the optical axis, g_{11} and g_{33} — the components of the gyration tensor g_{ij} , V — the half of the angle between the optical axes and λ — the vacuum light wavelength.

Making use of the matrices describing the gyration tensor g_{ij} , linear electrogyration tensor γ_{ijkl} and the tensor describing square electrogyration Π_{ijkl} [23–25], and taking into account the fact that in the ferroelectric phase of RS and DRS $P_1 = P_s$, the gyration G can be expressed as

$$G = g_{11}l_1^2 + g_{22}l_2^2 + g_{33}l_3^2 + 2\gamma_{14}l_2l_3P_s + \Pi_{11}l_1^2P_s^2 + \Pi_{12}l_2^2P_s^2 + \Pi_{13}l_3^2P_s^2, \quad (2)$$

where l_i are the direction cosines of the wave normal of the light.

In the ferroelectric phase the indicatrix of the light refractive indices rotates about the x -axis by an angle $\pm\varphi_s$ as a result of the linear electrooptical effect

induced by the spontaneous polarization. The optical plane makes an angle φ_s with the plane (010), which means that all three direction cosines will be different from zero: $l_1 = \cos V$, $l_2 = \sin V \sin(\pm\varphi_s)$, and $l_3 = \sin V \cos(\pm\varphi_s)$. The gyration surface and the indicatrix rotate synchronously [8]. For a small angle φ_s we can write

$$\varphi_s = a_1 P_s. \quad (3)$$

The a_1 coefficient, according to the relation given in [12, 26–28], can be written as

$$a_1 = \frac{\gamma_{14}}{g_{22} - g_{33}} = \frac{r_{14} n_2^2 n_3^2}{n_3^2 - n_2^2}, \quad (4)$$

where r_{14} and γ_{14} describe the linear electrooptical and linear electrogyration effects, n_2 and n_3 denote the light refractive indices along the axes y and z , g_{22} and g_{33} are the components of the gyration tensor g_{ij} (see for details papers [26–28]).

According to Eq. (3), the gyration G in the ferroelectric phase can be written as

$$G = g_{11} \cos^2 V + g_{33} \sin^2 V + P_s^2 g_{22} a_1^2 \sin^2 V + 2P_s^2 \gamma_{14} a_1 \sin^2 V \\ + P_s^2 \Pi_{11} \cos^2 V + P_s^2 \Pi_{13} \sin^2 V + P_s^4 \Pi_{12} a_1^2 \sin^2 V. \quad (5)$$

Thus, taking into account Eqs. (1), (4), and (5) the spontaneous optical rotatory power ρ_s along the optical axis in RS and DRS crystals can be written as

$$\rho_s = \Pi_{\text{ef}} P_s^2 + \Gamma_{\text{ef}} P_s^4, \quad (6)$$

where

$$\Pi_{\text{ef}} = \frac{\pi}{\lambda n_0} \left[\frac{3g_{22} - 2g_{33}}{(g_{22} - g_{33})^2} \gamma_{14}^2 \sin^2 V + \Pi_{11} \cos^2 V + \Pi_{13} \sin^2 V \right] \quad (7)$$

is the effective coefficient of the spontaneous electrogyration determining the magnitude of the contributions of the second order with respect to P_s and

$$\Gamma_{\text{ef}} = \frac{\pi \gamma_{14}^2 \Pi_{12} \sin^2 V}{\lambda n_0 (g_{22} - g_{33})^2} \quad (8)$$

is the effective coefficient of the spontaneous electrogyration determining the magnitude of the contributions of the fourth order with respect to P_s . Neglecting the fourth order contributions in Eq. (6), as it was proposed by Aizu [29] in his phenomenological description of OA, and taking into account that for the crystals showing continuous phase transition $P_s \propto (T_c - T)^{1/2}$ [30], we arrive at

$$\rho_s \propto (T_{c_2} - T). \quad (9)$$

The spontaneous optical rotatory power of RS and DRS_{II} is a linear function of $(T_{c_2} - T)$ within the limits of experimental uncertainty. This relation is fulfilled in the temperature ranges of $(T_{c_2} - T) = 20$ K for RS and $(T_{c_2} - T) = 25$ K for DRS_{II} (see Fig. 4), which means that relation (9) is held for these crystals.

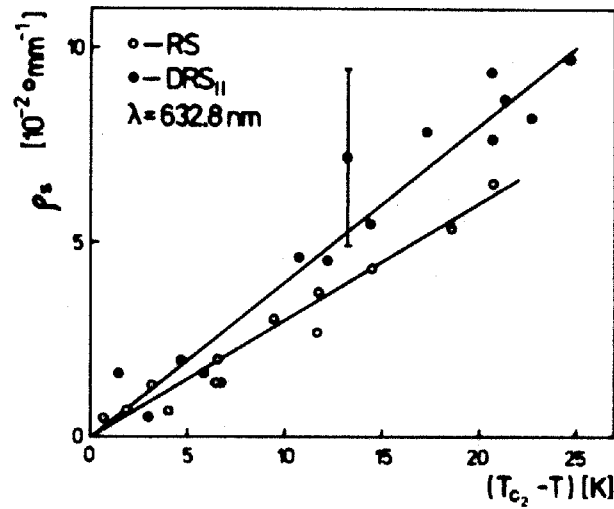


Fig. 4. The spontaneous optical rotatory power versus $(T_{c_2} - T)$ for RS and DRS_{II} crystals.

In view of the above, the RS and DRS crystals can be classified as belonging to the group of ferroelectrics for which the spontaneous optical rotatory power is proportional to the square of the spontaneous polarization. It has been shown that for these crystals the relation (9) is fulfilled, which means that they belong to the class of hipergyroelectrics, confirming the Aizu postulates [29].

4. Conclusion

- (i) The changes of the OA of the RS and DRS crystals induced by an external electric field can be described by the butterfly-type hysteresis loop and the sign of ρ does not change when the sense of the electric field is reversed. These findings evidence that the antipolar domains of both crystals studied are not enantiomorphic and are united by the hemitrope twin mechanism.
- (ii) The temperature dependence of ρ shows a continuous behaviour when the crystal passes the transition point in agreement with other experimental observations.
- (iii) The spontaneous optical rotatory power ρ_s of RS and DRS is quite small and charged with high uncertainty, however, it was established that ρ_s in the first approximation depends on the square of P_s .
- (iv) It was found that the relation $\rho_s \propto (T_{c_2} - T)$ is fulfilled for both crystals studied, which means that they belong to the hipergyroelectric class as postulated by Aizu [29].

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