

Photoelastic Behavior of Rochelle Salt

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All 12 stress-optic constants and all 12 strain-optic constants of Rochelle salt have been determined for the first time, by employing different experimental techniques at the different stages of the investigations. The values of q_{ij} and p_{ij} for the sodium yellow light at room temperature (27°C) are as follows:

$$\begin{aligned} q_{11} &= 3.1, & q_{21} &= 5.4, & q_{31} &= 5.0, & q_{44} &= -2.5(-0.9), \\ q_{12} &= 3.4, & q_{22} &= 0.76, & q_{32} &= 2.9, & q_{55} &= +1.5(+1.9), \\ q_{13} &= 3.2, & q_{23} &= 2.1, & q_{33} &= 1.6, & q_{66} &= -2.5(-1.7), \end{aligned}$$

all in units of 10^{-13} cm²/dyn;

$$\begin{aligned} p_{11} &= 0.35, & p_{21} &= 0.37, & p_{31} &= 0.36, & p_{44} &= -0.030(-0.011), \\ p_{12} &= 0.41, & p_{22} &= 0.28, & p_{32} &= 0.35, & p_{55} &= +0.0046(+0.0058), \\ p_{13} &= 0.42, & p_{23} &= 0.34, & p_{33} &= 0.36, & p_{66} &= -0.25(-0.017). \end{aligned}$$

The values inside the parentheses are those obtained by Pockels, and indicate only the orders of magnitude.

INTRODUCTION

ROCHELLE salt is a piezoelectric crystal. It belongs to the D_2 class of the orthorhombic system and possesses many interesting properties. Its elastic, piezoelectric, and dielectric properties have been extensively studied because of their many practical applications. The data are summarized with a critical discussion by Cady.¹ Mandell² has studied not only Rochelle salt as such, in regard to its elastic constants, but also the salt resulting after replacing the potassium ion by the ammonium ion. Since in a number of ways the behavior of Rochelle salt is very peculiar, several of its other physical properties such as the Raman effect and the linear and quadratic electro-optic effects have also been studied. Rochelle salt is optically active, the magnitude of rotation for sodium yellow light being 1.35 deg/mm

along each optical axis, according to Pocklington³ and Dufet.⁴

Pockels⁵ was the first to study the photoelastic behavior of Rochelle salt. However, he determined only the order of magnitude of three out of the 12 constants, namely, q_{44} , q_{55} , and q_{66} .

EXPRESSIONS RELATING q_{ij} AND STRESS BIREFRINGENCE

Since Rochelle salt belongs to the orthorhombic system at a room temperature of 27°C, it has 12 independent nonvanishing stress-optic constants and 12 independent nonvanishing strain-optic constants which are given in Pockels's scheme by the following matrices of q_{ij} and p_{ij} in the two-suffix notation:

$$\begin{pmatrix} q_{11} & q_{12} & q_{13} & 0 & 0 & 0 \\ q_{21} & q_{22} & q_{23} & 0 & 0 & 0 \\ q_{31} & q_{32} & q_{33} & 0 & 0 & 0 \\ 0 & 0 & 0 & q_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & q_{55} & 0 \\ 0 & 0 & 0 & 0 & 0 & q_{66} \end{pmatrix}, \quad \begin{pmatrix} p_{11} & p_{12} & p_{13} & 0 & 0 & 0 \\ p_{21} & p_{22} & p_{23} & 0 & 0 & 0 \\ p_{31} & p_{32} & p_{33} & 0 & 0 & 0 \\ 0 & 0 & 0 & p_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & p_{55} & 0 \\ 0 & 0 & 0 & 0 & 0 & p_{66} \end{pmatrix}.$$

It is well known that the amount of stress birefringence produced in a crystal depends upon the direction of the stress applied and the direction of observation through the crystal, as well as the nature of the stress (linear, tangential, or hydrostatic). Starting from first principles, one can obtain, as shown by Eppendahl⁶ for topaz, a relation between the observed stress bire-

fringence, direction of stress, direction of observation, and the photoelastic constants in Pockels's scheme. Table I summarizes such relationships among the several parameters.

EXPERIMENTAL DETAILS

(i) *Relative path retardations.* Rochelle salt has both optical activity and natural birefringence, but even the smallest value of its natural birefringence that occurs for observations along the X axis is very large compared with its optical activity. It is only when optical activity and birefringence are of the same order of magnitude that it becomes difficult to estimate the

¹ W. G. Cady, *Piezoelectricity* (McGraw-Hill Book Co., New York, 1946).

² W. Mandell, Proc. Roy. Soc. (London) **A116**, 623 (1927).

³ H. C. Pocklington, Phil. Mag. **2**, 361 (1901).

⁴ H. Dufet, J. Phys. **3**, 757 (1904).

⁵ F. Pockels, *Lehrbuch der Kristallographie* (B. G. Teubner, Leipzig, 1906).

⁶ B. R. Eppendahl, Ann. Physik **61**, 595 (1920).

TABLE I. Expressions for stress birefringence in Rochelle salt.

Direction of stress ^a	Direction of observation ^a	Nature of observation	Expression for path retardation
[100]	[001]	absolute	$(n_x^3 q_{11} - 2n_x s_{13})$ for vertical vibrations
[100]	[001]	absolute	$(n_y^3 q_{21} - 2n_y s_{13})$ for horizontal vibrations
[100]	[001]	relative	$\frac{1}{2}(n_x^3 q_{11} - n_y^3 q_{21}) + s_{13}(n_y - n_x)$
[100]	[010]	relative	$\frac{1}{2}(n_x^3 q_{11} - n_z^3 q_{31}) + s_{12}(n_z - n_x)$
[010]	[100]	absolute	$(n_y^3 q_{22} - 2n_y s_{12})$ for vertical vibrations
[010]	[100]	absolute	$(n_z^3 q_{32} - 2n_z s_{12})$ for horizontal vibrations
[010]	[100]	relative	$\frac{1}{2}(n_y^3 q_{22} - n_z^3 q_{32}) + s_{12}(n_z - n_y)$
[010]	[001]	relative	$\frac{1}{2}(n_y^3 q_{22} - n_x^3 q_{12}) + s_{23}(n_x - n_y)$
[001]	[100]	absolute	$(n_z^3 q_{33} - 2n_z s_{13})$ for vertical vibrations
[001]	[100]	absolute	$(n_y^3 q_{23} - 2n_y s_{13})$ for horizontal vibrations
[001]	[100]	relative	$\frac{1}{2}(n_z^3 q_{33} - n_y^3 q_{23}) + s_{13}(n_y - n_z)$
[001]	[010]	relative	$\frac{1}{2}(n_z^3 q_{33} - n_x^3 q_{13}) + s_{23}(n_x - n_z)$
[100]	<i>M</i> or <i>M'</i>	relative	$\frac{1}{2}n_x^3 q_{11} - \frac{1}{4}n_y z^3 (q_{21} + q_{31}) - \frac{1}{2}(n_x - n_y z)(s_{12} + s_{13})$
[010]	<i>L</i> or <i>L'</i>	relative	$\frac{1}{2}n_y^3 q_{22} - \frac{1}{4}n_x z^3 (q_{32} + q_{12}) - \frac{1}{2}(n_y - n_x z)(s_{21} + s_{23})$
[001]	<i>N</i> or <i>N'</i>	relative	$\frac{1}{2}n_z^3 q_{33} - \frac{1}{4}n_x y^3 (q_{13} + q_{23}) - \frac{1}{2}(n_z - n_x y)(s_{31} + s_{32})$
<i>M</i>	<i>M'</i>	relative	$\frac{1}{4}n_y z^3 (q_{22} + q_{23} + q_{32} + q_{33} + 2q_{44}) - \frac{1}{4}n_x z^3 (q_{12} + q_{13}) - \frac{1}{4}(n_y z - n_x)(s_{22} + 2s_{23} + s_{33} - s_{44})$
<i>L</i>	<i>L'</i>	relative	$\frac{1}{4}n_x z^3 (q_{11} + q_{13} + q_{31} + q_{33} + 2q_{55}) - \frac{1}{4}n_y z^3 (q_{21} + q_{23}) - \frac{1}{4}(n_x z - n_y)(s_{11} + 2s_{13} + s_{33} - s_{55})$
<i>N</i>	<i>N'</i>	relative	$\frac{1}{4}n_x y^3 (q_{11} + q_{12} + q_{21} + q_{22} + 2q_{66}) - \frac{1}{4}n_z^3 (q_{31} + q_{32}) - \frac{1}{4}(n_x y - n_z)(s_{11} + 2s_{12} + s_{22} - s_{66})$

^a *M* indicates the direction equally inclined to *Y* and *Z* in the *YZ* plane; *L* indicates the direction equally inclined to *Z* and *X* in the *ZX* plane; and *N* indicates the direction equally inclined to *X* and *Y* in the *XY* plane. *M'*, *L'*, *N'* are perpendicular to *M*, *L*, and *N*, respectively.

one in the presence of the other, as was shown by Ramaseshan⁷ in determining the Faraday rotation in corundum. The Poincaré sphere representation can be adopted to determine the artificial birefringence in the presence of optical activity when they are of similar order of magnitude, as Ramachandran and Chandrasekharan⁸ did in studying the photoelastic behavior of sodium chlorate. Since the optical activity of Rochelle salt is very small compared with its natural birefringence, the Babinet compensator has been employed to determine the small additional birefringence caused by mechanical stress, as was done by Mueller⁹ to study the Kerr electro-optic effect in Rochelle salt.

(ii) *Absolute path retardations.* The method of localized fringes enables one to determine absolute path retardations caused by stress. Here the crystal itself is used as an interferometer by forming localized interference fringes in the crystal, as employed originally by Peters¹⁰ for studying the variation of refractive index with temperature for optical glasses. This method was followed by Ramachandran for studying the photoelastic¹¹ and thermo-optic¹² behavior of diamond. Radhakrishnan¹³ used the same technique to study the variation of the refractive index of quartz with temperature for ordinary rays by transmitted localized fringes in a plate perpendicular to the optic axis.

⁷ S. Ramaseshan, Proc. Indian Acad. Sci. **A34**, 32 (1951); **A34**, 97 (1951).

⁸ G. N. Ramachandran and V. Chandrasekharan, Proc. Indian Acad. Sci. **A33**, 199 (1951).

⁹ Hans Mueller, Phys. Rev. **47**, 175 (1935).

¹⁰ C. G. Peters, J. Res. Nat. Bur. Std. **20**, 635 (1926).

¹¹ G. N. Ramachandran, Proc. Indian Acad. Sci. **A25**, 208 (1947).

¹² G. N. Ramachandran, Proc. Indian Acad. Sci. **A25**, 266 (1947).

¹³ T. Radhakrishnan, Proc. Indian Acad. Sci. **A27**, 44 (1948).

This method of localized interference fringes was applied in the present investigations to determine the variation of index of refraction with mechanical stress, yielding the absolute values of q_{11} , q_{31} , q_{12} , q_{22} , q_{23} , and q_{33} . One significant fact may be mentioned in this connection. In the case of Faraday rotation, plane polarized light has its plane of vibration rotated by a magnetic field; if the light is now reflected at the rear surface, the rotation of the plane of polarization is doubled. In the case of optical activity, however, the reflected beam suffers an opposite rotation of equal magnitude and hence emerges from the first face without any rotation. Thus the front- and back-reflected beams interfere, as if the medium was optically inactive, forming the usual localized interference fringes. The validity of this method is based on this result. It may be noted that the Jamin interferometer adopted by Eppendahl⁶ for measuring the absolute retardations in topaz under mechanical stress cannot be used here because of the influence of optical activity on interference fringes. The values of q_{ij} obtained by the method of localized interference fringes may not be very accurate, as has already been discussed by Bhagavantam and Suryanarayana¹⁴ and by Vedam.¹⁵ Hence the observations made with the Babinet compensator are coupled with those made with localized fringes in order to give due weight to both sets of observations and thus arrive at the individual values of the related q_{ij} .

(iii) *Ultrasonic method.* Mueller¹⁶ has shown how the study of ultrasonic diffraction patterns could lead to the determination of the elasto-optic ratios of cubic

¹⁴ S. Bhagavantam and D. Suryanarayana, Proc. Indian Acad. Sci. **A26**, 97 (1947); Acta Cryst. **2**, 26 (1949); **2**, 81 (1949).

¹⁵ K. Vedam, Proc. Indian Acad. Sci. **A34**, 161 (1951).

¹⁶ Hans Mueller, Z. Krist. **99**, 122 (1938).

crystals. The ultrasonic method was suitably extended by the author¹⁷ to noncubic crystals such as calcite, quartz, and barite. This method was adopted here to obtain the ratios of the elasto-optic constants of Rochelle salt, thereby affording an independent check on the results obtained by optical methods followed in (i) and (ii) above. Thus, in the present investigations, all the three methods above were adopted.

(iv) *Preparation of crystal specimens.* Single crystals of Rochelle salt were grown by the method of slow evaporation of nearly saturated aqueous solution, using concentrated sulphuric acid as the drying agent. In order to get fairly large specimens, seeding was found to be essential, otherwise a large crop of tiny crystals resulted. By the method of seeding, specimens with dimensions $8 \times 8 \times 5$ cm could easily be grown in the laboratory. All the specimens used were flawless with the usual prominent faces and pinacoids well developed, so that the axes could easily be determined using a contact goniometer and confirmed by examination between crossed polaroids. The crystallographic data provided by Cady¹ were used to identify the faces and axes.

Because the Rochelle salt crystal was soft, it could be cut with a jeweller's saw, using kerosene as a lubricant. The grinding was done entirely by hand, using fine carborundum powder on a plane sheet of glass, with kerosene as lubricant. No apparatus were employed to give the required orientations. Instead, a contact goniometer was employed to give the required orientation for cutting and grinding, and in the final stages, the prism, so cut and ground, was placed on a plane sheet of glass and reflection tests were used to ensure perpendicularity between the different pairs of faces. The orientations of the prisms were accurate to within 1° . Before the prism was taken to the polishing tool for receiving the optical polish, its faces were ground on a piece of ground glass and subsequently on an ordinary glass plate with polished surfaces, again using kerosene as lubricant. During this stage the faces received a little polish which helped in testing the plane parallelism of the faces.

Considerable time was spent on developing suitable techniques for polishing this soft crystal. The method finally adopted was as follows: Jeweller's rouge powder is cooked with beeswax, mixing it thoroughly all the while. Fine silk cloth, slightly and evenly worn, is soaked in this wax and the soaked cloth is stretched tightly over a warm brass base. When the brass tool is slightly warm, the surface of the cloth is pressed by an electric iron and it is then allowed to cool. After cooling, the surface of the cloth is finally prepared for the job by polishing the surface of a spare specimen crystal.

The raw crystals, as well as the optically polished prisms, were kept in an air-tight desiccator with no drying agent inside. The optical polish on the prisms is well retained when the humidity is maintained at the

TABLE II. Rochelle salt: Dimensions of prisms employed.

No. of prism	Length		Breadth		Thickness	
	Parallel to ^a	mm	Parallel to ^a	mm	Parallel to	mm
1	[100]	8.57	[001]	5.40	[010]	5.80
2	[010]	10.95	[100]	5.17	[001]	5.74
3	[001]	12.98	[010]	5.30	[100]	4.82
4	[100]	12.34	[010]	4.95	[001]	4.65
5	[010]	12.65	[001]	5.50	[100]	6.35
6	[001]	11.56	[010]	6.35	[100]	5.78
7	<i>M</i>	11.65	<i>M'</i>	5.10	[100]	6.25
8	<i>L</i>	12.32	<i>L'</i>	4.35	[010]	5.50
9	<i>N</i>	11.53	<i>N'</i>	3.89	[001]	6.30
10	[100]	10.32	[010]	3.33	[001]	5.20
11	[010]	11.05	[001]	2.98	[100]	5.21
12	[001]	10.23	[100]	3.32	[010]	4.76

^a The directions *M*, *L*, and *N* have the same significance as in Table I.

optimum range at room temperature (Mason¹⁸); thus during the progress of the experiment, the humidity in the room was maintained within the range with basins of concentrated sulphuric acid. Maintenance of humidity within the range is absolutely essential, since for optical work good optical polish of the transmitting faces is the primary criterion.

OBSERVATIONS AND RESULTS

The following are the observations and results obtained by the author¹⁹ on Rochelle salt.

The values of the several constants that enter the calculations are as follows:

(i) Principal refractive indices at 20°C for sodium yellow light are $n_x = 1.4954$, $n_y = 1.4920$, and $n_z = 1.4900$ (from Cady's *Piezoelectricity*¹).

(ii) Elastic constants: $c_{11} = 4.25$, $c_{22} = 5.15$, $c_{33} = 6.29$, $c_{44} = 1.25$, $c_{55} = 0.304$, $c_{66} = 0.996$, $c_{12} = 2.96$, $c_{23} = 3.42$, and $c_{13} = 3.57$ (all in units of 10^{11} dyn/cm²); $s_{11} = 51.8$,

TABLE III. Observations on differential birefringence.

No.	Expressions for birefringence	Relative path retardation (10^{-13} cm ² /dyn)
1	$\frac{1}{2}(n_x^3 q_{11} - n_z^3 q_{31})$	-3.4
2	$\frac{1}{2}(n_x^3 q_{11} - n_y^3 q_{21})$	-3.8
3	$\frac{1}{2}(n_y^3 q_{22} - n_x^3 q_{12})$	-4.4
4	$\frac{1}{2}(n_y^3 q_{22} - n_z^3 q_{32})$	-3.6
5	$\frac{1}{2}(n_x^3 q_{33} - n_y^3 q_{23})$	-0.8
6	$\frac{1}{2}(n_x^3 q_{33} - n_z^3 q_{13})$	-2.6
7	$\frac{1}{2}n_{xy}^3(q_{11} + q_{12} + q_{21} + q_{22} + 2q_{66}) - \frac{1}{4}n_x^3(q_{31} + q_{32})$	-3.5
8	$\frac{1}{2}n_{xz}^3(q_{11} + q_{13} + q_{31} + q_{33} + 2q_{55}) - \frac{1}{4}n_y^3(q_{21} + q_{23})$	+0.44
9	$\frac{1}{2}n_{yz}^3(q_{22} + q_{23} + q_{32} + q_{33} + 2q_{44}) - \frac{1}{4}n_x^3(q_{12} + q_{13})$	-4.5

¹⁸W. P. Mason, *Piezoelectric Crystals* (D. Van Nostrand Co., New York, 1950).

¹⁹T. S. Narasimhamurthy, Ph.D. thesis, Osmania University, Hyderabad, India, 1955 (unpublished).

¹⁷T. S. Narasimhamurthy, *Acta Cryst.* **14**, 1176 (1961).

TABLE IV. q_{ij} data from absolute interferometers.

No.	Expression	Absolute path retardation (10^{-13} cm ² /dyn)
1	$n_x^3 q_{11}$	10.3
2	$n_z^3 q_{31}$	16.7
3	$n_y^3 q_{22}$	2.65
4	$n_x^3 q_{12}$	11.1
5	$n_z^3 q_{33}$	5.50
6	$n_y^3 q_{23}$	7.08

$s_{22}=34.8, s_{33}=33.4, s_{44}=79.8, s_{55}=328, s_{66}=101, s_{12}=-15.3, s_{23}=-10.3,$ and $s_{13}=-21.1$ (all in units of 10^{-13} cm²/dyn). The above elastic constants are those obtained by Mason and reported by Cady.¹ The dimensions of the prisms are given in Table II, and the observations on differential birefringence yield the data in Table III. Observations on absolute interferometer (by the method of localized interference fringes on prisms 10, 11, 12) yielded for q_{ij} the results in Table IV.

Remarks. From the results given in Table IV, as obtained by the method of localized fringes, we have $n_x^3 q_{11} - n_z^3 q_{31} = -6.45$, whereas from the Babinet compensator measurements, $n_x^3 q_{11} - n_z^3 q_{31} = -6.80$. The agreement should be considered fairly good, in view of the fact that a slight alteration of the assumed values of s_{12}, s_{23} , and s_{13} considerably alters the calculated value of q_{ij} from the measurements on the absolute path retardation. A similar difficulty was met by Vedam,¹⁵ in the case of barite especially for stress along the Z axis and observation along the X axis.

Similarly, the localized-fringes method yields $n_y^3 q_{22} - n_x^3 q_{12} = -8.47$, whereas by Babinet observations $n_y^3 q_{22} - n_x^3 q_{12} = -8.8$, and $n_z^3 q_{33} - n_y^3 q_{23} = -1.58$ by the localized-fringes method and -1.6 by Babinet observations. Thus, in the light of observations made earlier,¹⁵ the observations by the Babinet compensator are coupled with those by the method of localized fringes,

TABLE V. Results from ultrasonic studies on Rochelle salt.

Direction of excitation	Direction of observation	Expression for R	θ	Numerical value Ultrasonic experiments	Optical experiments
1	[100]	p_{31}/p_{11}	49°	1.15	1.08
2	[100]	p_{21}/p_{11}	50°	1.19	1.1
3	[010]	p_{12}/p_{22}	55°	1.43	1.5
4	[010]	p_{32}/p_{22}	49°	1.15	1.25
5	[001]	p_{23}/p_{23}	43°	0.93	0.94
6	[001]	p_{13}/p_{33}	52°	1.28	1.17

in order to give due weight to both sets of observations and thus arrive at the individual values of the related q_{ij} .

The values of q_{ij} and p_{ij} thus calculated from the above optical measurements are given below; the values of q_{ij} and p_{ij} are correct to within 10%:

$$q_{11}=3.1, q_{21}=5.4, q_{31}=5.0, q_{44}=-2.5(-0.9),$$

$$q_{12}=3.4, q_{22}=0.76, q_{32}=2.9, q_{55}=+1.5(+1.9),$$

$$q_{13}=3.2, q_{23}=2.1, q_{33}=1.6, q_{66}=-2.5(-1.7),$$

(all in units of 10^{-13} cm²/dyn);

$$p_{11}=0.35, p_{21}=0.37, p_{31}=0.36, p_{44}=-0.030(-0.011),$$

$$p_{12}=0.41, p_{22}=0.28, p_{32}=0.35, p_{55}=+0.0046(+0.0058),$$

$$p_{13}=0.42, p_{23}=0.34, p_{33}=0.36, p_{66}=-0.025(-0.017).$$

The values in brackets are those determined by Pockels, and indicate only the order of magnitude.

Observations on the ultrasonic behavior of single crystals of Rochelle salt have yielded the results collected in Table V.

The observations under θ are those obtained after allowing for the finite amplitude of the ultrasonic excitation and for the optical activity²⁰ of Rochelle salt. The agreement between the two sets of values may be considered fairly good.

Effect of hydrostatic pressure on Rochelle salt. Here the six pressure components can be written $P_{xx}=P_{yy}=P_{zz}=P; P_{xy}=P_{yz}=P_{zx}=0$. Let the optical parameters of the crystal in the unstressed and stressed conditions be represented by B_{ij}^0 and B_{ij} , respectively. Then according to Pockels's phenomenological theory of photoelasticity, we have

$$B_{11} - B_{11}^0 = -P(q_{11} + q_{12} + q_{13}) = -P \times 9.70 \times 10^{-13},$$

$$\Delta n_x = 1.62 \times 10^{-3}/\text{kbar};$$

$$B_{22} - B_{22}^0 = -P(q_{21} + q_{22} + q_{23}) = -P \times 8.26 \times 10^{-13},$$

$$\Delta n_y = 1.37 \times 10^{-3}/\text{kbar};$$

$$B_{33} - B_{33}^0 = -P(q_{31} + q_{32} + q_{33}) = -P \times 9.50 \times 10^{-13},$$

$$\Delta n_z = 1.57 \times 10^{-3}/\text{kbar}.$$

All the principal refractive indices increase under hydrostatic pressure, as in the case of barite and topaz.

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²⁰ K. Vedam and G. N. Ramachandran, Proc. Indian Acad. Sci. A34, 240 (1951).