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Polymorphism of Rochelle Salt

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A careful analysis of the properties of Rochelle salt leads to the conclusion that this crystal belongs to the *monoclinic hemimorphic* symmetry class between the so-called Curie points (+23.7°C and −18°C), whereas it is orthorhombic hemihedric at other temperatures. The Curie points are to be regarded as crystallographic inversion points like the high-low inversion points in quartz and other crystals. Dielectric anomalies as observed for Rochelle salt must be expected near inversions from a pyroelectric to a nonpyroelectric crystal glass. Other properties of Rochelle salt discussed in the light of the new classification are the electrooptic effect, the converse and the direct piezoelectric effect, and the specific heat. A comparison with symmetry conditions in ferromagnetic crystals is made.

I. INTRODUCTION

THE anomalous dielectric behavior of Rochelle salt between −18°C and +23.7°C, and the discontinuities observed at these two points show a close analogy to ferromagnetism and its transition to paramagnetism at the Curie point.[1–3] These characteristic temperatures have therefore been called the lower and the upper Curie points of Rochelle salt.

It is the purpose of this paper to deduce from well-known physical properties that at these temperatures crystallographic inversions occur in Rochelle salt, and that it belongs to the *hemimorphic* class of the *monoclinic* system (sphenoidal class, C_2) *between* the Curie points, whereas there is no reason to question its *orthorhombic hemihedral* symmetry (rhombic-bisphenoidal class, V) at other temperatures.

II. CRYSTALLOGRAPHIC MEASUREMENTS

These conclusions have hitherto not been drawn because Rochelle crystals, whether grown above or below the upper Curie point, *appear* to possess orthorhombic symmetry. This, the accepted classification, is confirmed, within the limits of experimental precision, by goniometric measurements[4] and x-ray analysis.[5, 6] Even the space group has been determined as V^3. All these measurements were carried out at room temperature, i.e., between the Curie points, though the crystals had probably been grown at higher temperatures in most cases.

III. PHYSICAL PROPERTIES OF LOWER SYMMETRY

However, a variety of physical experiments have led to an interpretation[2d, 3, 7] of the electric behavior of Rochelle salt which, as will be shown in this paper, is in contradiction to orthorhombic hemihedric symmetry for temperatures between the Curie points. It is now agreed that in this range a Rochelle crystal consists of regions having a *spontaneous electric moment*, analogous to the Weiss regions in ferromagnetic metals. The electric moments are, however, always parallel to the crystallographic *a* axis. It depends on mechanical stresses or other accidental circumstances which of the two possible orientations the moment will have in any region in the crystal. Regions of opposite polarization are in general not balanced, thus giving rise to a polarity of the crystal as a whole.

Unipolar conductivity,[1c] asymmetry in the dielectric polarizibility[1b, 2c] and in the converse piezoelectric effect,[8] and also a pyroelectric effect[1c, 3] have indeed been measured. With the powder test for pyroelectricity, Mueller succeeded in making the single regions visible; their dimensions are of the order of 1 cm.

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[1] (a) J. Valasek, Phys. Rev. **17**, 475 (1921); (b) **19**, 478 (1922); (c) **20**, 639 (1922).

[2] (a) P. Kobeko and I. Kurtschatov, Zeits. f. Physik **66**, 192 (1930); (b) B. Kurtschatov and I. Kurtschatov, Physik Zeits Sowjetunion **3**, 321 (1933); (c) I. Kurtschatov, Physik Zeits Sowjetunion **4**, 125 (1933); (d) **5**, 200 (1934).

[3] H. Mueller, Phys. Rev. **47**, 175 (1935).

[4] See P. Groth, *Physikalische Krystallographie* (Leipzig, 1905), p. 392.

[5] B. E. Warren and H. M. Krutter, Phys. Rev. **43**, 500 (1933).

[6] H. Staub, Helv. Phys. Acta **7**, 3 (1934).

[7] H. Staub, Naturwiss. **23**, 728 (1935).

[8] (a) I. Vigness, Phys. Rev., **46**, 255 (1934); (b) **48**, 198 (1935).

Smaller crystals are often a single region. The magnitude of the spontaneous polarization is best obtained from the polarization cycle with low frequency a.c. It has a flat maximum of about 600 e.s.u.$=20\times10^{-8}$ coul./cm^2 near 0°C, and falls off to zero as either Curie point is approached.[3, 9]

No unipolarities or other signs of a spontaneous moment are present above the upper or below the lower Curie point.

IV. CRYSTALLOGRAPHIC CONCLUSION

The only correct crystallographic description of this behavior is the following. Between the Curie points the a axis is a polar axis; consequently the b and c axes are no longer axes of symmetry. With only one twofold axis of symmetry left the crystal belongs to the *hemimorphic* class of the *monoclinic* system. The apparent orthorhombic symmetry is a "pseudosymmetry."[10] Large specimens are twins; the b or the c axis can be regarded as twinning axis. The Curie points are *inversion points* to orthorhombic hemihedric symmetry.

The polymorphism of Rochelle salt is a typical case of *polysyngony*,[11] for which the high-low inversions of *quartz* and *cristobalite* are classical examples. The twinning of monoclinic Rochelle salt corresponds to the Dauphiné, or orientational, twinning shown by low quartz prepared by cooling from uniform high quartz.[12] For low-cristobalite, as for monoclinic Rochelle salt, the deviations of the geometrical forms from the higher symmetry are so small that they could not be detected by x-ray measurements.[13] Here, as for most other inversions of the polysyngonic type, it was the sudden disappearance of optical double refraction which revealed the inversion.

V. HYPOTHESES OF OTHER AUTHORS

In one of his early papers *Valasek* (reference 1c, p. 660) points out that a pyroelectric effect in the orthorhombic-hemihedric class is forbidden by *Neumann's principle;* he therefore questions the unconditional validity of this fundamental principle of crystal physics. At the same time Valasek discusses the possibility that Rochelle salt belongs to the *orthorhombic-hemimorphic* class; he finds it impossible because for this class the piezoelectric constant d_{14}, which is very high in Rochelle salt, should vanish. We may add that the orthorhombic-hemimorphic class has a plane of symmetry, whereas the absence of such a plane in Rochelle crystals was known to *Pasteur* more than 80 years ago.[14] Nevertheless, the same question was recently discussed again by *Taschek and Osterberg*,[15] of course with the same result.

Mueller tries to overcome the dilemma by the following remark (ref. 3, p. 180): "The crystallographic symmetry of Rochelle salt does not permit an ordinary pyroelectric effect. Its apparent pyroelectricity is due to this[16] spontaneous polarization. The existence of this effect is therefore no violation of Neumann's principle."

We cannot agree with Mueller's differentiation of "apparent" and "ordinary" pyroelectricity. Unless a "false effect of the first kind," i.e., produced by nonuniform heating, pyroelectricity is always due to a spontaneous electric moment necessarily linked with an interior field. It has to be taken into account in the determination of the symmetry class, irrespective of the insight we may or may not have into the molecular origin of the polarization.

VI. THE CONVERSE PIEZOELECTRIC EFFECT OF THE INTERIOR FIELD

It is possible to deduce indirectly from experimental data that between the Curie points the *geometrical* form of Rochelle salt as well as the physical properties exhibits monoclinic symmetry only. Measurements on the converse piezoelectric effect[8] show that a reversal of the spontaneous polarization, as achieved by an electric field parallel to the a axis, is accompanied by a shearing deformation y_z which amounts to about 16×10^{-4} between 0°C and +10°C. This corre-

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[9] C. B. Sawyer, and C. H. Tower, Phys. Rev. **35**, 269 (1930).

[10] Groth (reference 4), p. 271.

[11] For a definition of this term see T. F. W. Barth, Am. J. Sci., **27**, 273 (1934).

[12] R. B. Sosman, *The Properties of Silica* (New York 1927), p. 194.

[13] T. F. W. Barth, Am. J. Sci. **24**, 97 (1932).

[14] L. Pasteur. Ann. chim. phys. (3) **28**, 56 (1850).

[15] R. Taschek and H. Osterberg, Phys. Rev. **50**, 572 (1936).

[16] The quoted sentences are preceded by a theory of the electrical properties of Rochelle salt analogous to the Weiss theory of magnetism. See Section VII.

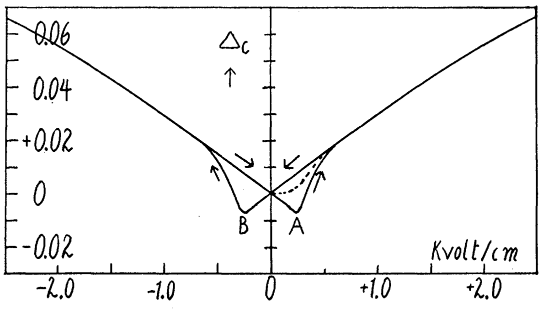

FIG. 1. Electrooptic effect for rays in the *c* direction; schematic, after *Mueller* (reference 3, Figs. 23 and 24). Temperature about +20°C. The ordinates give the increase in optic path length difference (in fractions of one wave-length per cm path) between the two linear light components. The abscissas are field strengths in the *a* direction. Dotted curve: virgin polarization.

sponds to a change in the angle between the *b* and *c* axes of 16×10^{-4} radians = 5.5′. The departure of the angle from 90° must be the same for both orientations of the polarization; at the temperature quoted, therefore, the *b and c axes intersect* at an angle different from 90° by 5.5′/2 or *at 89° 57.3′*. Only measurements of high precision, using *un-twinned* material, could directly detect this slight deviation from orthorhombic symmetry.

VII. RELATION TO MUELLER'S THEORY

H. Mueller's theory of Rochelle salt is based on the assumption that, between the Curie points, its "molecules" assume an electric moment parallel to and dependent upon an interior electric field, which in turn is maintained by this polarization.

There is no contradiction to our crystallographic results if Rochelle salt is regarded as built up of *unit cells* which would be orthorhombic if isolated, but which, between the Curie points, become polarized and slightly deformed under the influence of neighboring unit cells. Mueller only overlooked the fact that, as a consequence of his own assumptions, the *entire crystal* is not orthorhombic but monoclinic.

Mueller's theory is in quantitative accord with his dielectric and electrooptic measurements just *above* the upper Curie point; it yields the correct order of magnitude for these effects between the Curie points. The present crystallographic treatment does not provide quantitative predictions, but it gives a more direct qualitative interpretation of the effects between the Curie points, and is entirely free of any molecular assumptions. In the following sections various effects will be studied from both points of view.

VIII. DIELECTRIC POLARIZATION

In Mueller's theory, the dielectric hysteresis loop observed for Rochelle salt between the Curie points is a complete analog to the ferromagnetic hysteresis loop. The spontaneous polarization corresponds to remanent magnetism.

From the crystallographic point of view, this polarization is the pyroelectric moment present in all crystals of certain symmetry classes. Its reversal by the action of an electric field or of a mechanical shearing stress is a *reversal* of the *polar axis* of the crystal. The nearness of the transition points accounts for this effect in Rochelle salt. It has a parallel in the peculiar transformation under a shearing stress observed in calcite.[17] Both processes are internal movements which end in a state that is identical with the original state except for orientation in space. For both calcite and Rochelle salt the configuration midway between the stable states is of higher symmetry than the latter. As the temperature of Rochelle salt approaches the transition point, the stable states come nearer and nearer to the higher symmetry and the energy required to effect the reversal approaches zero. This means that the susceptibility for the *a* direction and the corresponding piezoelectric constant d_{14} approach infinity at the Curie points, as is indeed indicated by experiments.[3, 18]

IX. ELECTROOPTIC EFFECT

The symmetry of the orthorhombic hemihedric class does not permit a linear electrooptic effect of an electric field in the *a* direction for rays traveling along one of the crystallographic axes. The effects observed in these directions by *Pockels*[19] and by *Mueller*[3] have therefore been interpreted as *quadratic*, or *Kerr effects*. Indeed, they have the same sign for opposite directions of the field (Fig. 1); however the observed variation with the intensity of the field is *linear*

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[17] Groth (reference 4), pp. 245–250; Tutton, *Crystallography* (London, 1911), pp. 449–451.

[18] O. Norgorden, Phys. Rev. **49**, 820 (1936).

[19] F. Pockels, Göttinger Abhandl. **39**, 161 (1894).

below the upper Curie point, with an approach to saturation from 2.5 kv/cm upwards. Mueller's explanation is that the exterior field E produces only a relatively small addition ΔF to the spontaneous interior field F_0. The Kerr effect is proportional to $(F_0+\Delta F)^2 \approx F_0^2+2F_0\Delta F$. ΔF is in first approximation proportional to E. As the effect of F_0^2 is already included in the natural birefringence, the variation of the birefringence with the applied field is indeed linear.

The crystallographic interpretation is simply this: what is observed is really a *linear electro-optic effect*, which is no longer impossible for the direction studied if the crystal is regarded as monoclinic hemimorphic. Owing to the reversal of the polar axis when the field is sufficient to overcome the coercive force (points A, B, Fig. 1), the effect is the same for both directions of the field, but there is no discontinuity at zero field.

X. Electrostriction and Piezoelectric Effect

As *optic refractivity* and *strain* are represented by tensors of the same kind, the same symmetry relations as for the *Kerr effect* must hold for the *quadratic electrostriction.*

From the point of view of Mueller's theory, Rochelle salt would therefore be an orthorhombic hemihedric crystal in which, owing to the spontaneous polarization, the quadratic electrostriction, like the Kerr effect, depends linearly on the applied field if the temperature is between the Curie points. *Five* coefficients are needed to describe in an orthorhombic crystal all possible effects of such a combination of a spontaneous polarization along one of the axes and an applied field in an arbitrary direction.[20]

These five coefficients correspond exactly to the *five piezoelectric constants* which the *monoclinic hemimorphic* class has in addition to the three constants present for the orthorhombic hemihedric class.[21]

Before enumerating these we must adopt a convention concerning the crystal axes. It is usual to call the polar axis in a hemimorphic crystal the c axis. However, it seems expedient to retain the designation commonly employed with Rochelle salt, even when it becomes monoclinic hemimorphic. The axis of Rochelle salt generally known as a axis shall retain this name *although* it is a *polar* axis. Where a rectangular coordinate system is required, the X axis shall coincide with a, and the Y axis with b. The Z axis will then form an angle of a few minutes with the c axis (see Section VI). The system of piezoelectric constants is now obtained from that of Voigt[22] by exchanging the index 1 with 3, and 4 with 6, and rearranging the constants in the usual order. We thus have

$$\begin{matrix} d_{11} & d_{12} & d_{13} & d_{14} & 0 & 0 \\ 0 & 0 & 0 & 0 & d_{25} & d_{26} \\ 0 & 0 & 0 & 0 & d_{35} & d_{36}. \end{matrix}$$

An experimental search for the new constants would not decide in favor of either theory, as both Mueller's and the crystallographic point of view require their presence. As far as we know no attempt to find these constants has yet been made. It is true that Taschek and Osterberg[15] looked for a set of five new piezoelectric constants which might possibly take the place of the well-known constants d_{14}, d_{25}, d_{36}; but their search was, erroneously, for constants connected with a polarity of the c axis and not the a axis; their result has therefore no bearing on our problem.[22a]

XI. Specific Heat

At the upper Curie point of Rochelle salt an anomaly in the specific heat is observed, just as at the Curie points of ferromagnetic metals.[23] This effect has been regarded as one of the strongest arguments for the existence of a spontaneous polarization.[7]

From our crystallographic point of view we note that an anomaly of similar shape is observed at polysyngonic inversion points which are *not*

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[20] On the quadratic electrostriction in crystals see F. Pockels, in *Encyclopädie der Mathem. Wiss.* (Leipzig, 1906) vol. V/2, p. 360.

[21] The electrostrictive effect derived from Mueller's theory is the *converse* piezoelectric effect for monoclinic-hemim. symmetry; however the system of coefficients is the same for direct and converse effect.

[22] W. Voigt, *Lehrbuch der Kristallphysik* (Leipzig, 1910) (or second edition, 1928), p. 829.

[22a] *Note added in proof.* Since the completion of this paper H. Körner, Zeits. f. Physik **103**, 170 (1936), has published measurements which show the absence of other constants than d_{14}, d_{25}, d_{36} within his limits of error. However, these observations were made at temperatures so little below the upper Curie point that only very small values for the other constants could be expected from our theory.

[23] A. Rusterholz, Helv. Phys. Acta **8**, 39 (1935).

linked with the disappearance of a spontaneous electric moment, as for quartz.[24] One is therefore not justified in assuming that the anomalous specific heat of Rochelle salt is entirely due to the process of depolarization. Indeed, the observed discontinuous decrease in the specific heat at the transition point is more than 10 times greater than the value calculated from the electrical theory with Mueller's data for spontaneous polarization and interior field (reference 3, pp. 189, 191). Only from a detailed knowledge of the molecular rearrangement involved would a calculation of the specific heat be possible.

XII. RELATION TO TRANSITIONS IN OTHER CRYSTALS

A first step towards a *molecular theory* of Rochelle salt has been taken by R. H. Fowler.[25] His theory connects the anomalies in Rochelle salt, especially the lower Curie point, with the large group of recently discovered oscillation-rotation transitions.

Without in any way questioning this connection, or the analogy to ferromagnetism, we have here emphasized the relation of the Rochelle anomalies to a group of transitions which have long been recognized as crystallographic inversions, whereas little is known about their molecular dynamics. The similarity of the anomalous specific heat for these different groups of transitions leads to the assumption that they all can be explained by the same molecular fact, namely the breakdown of a *coöperative state* (in the terminology of Fowler).

We have to mention an early attempt of *Perrier* to correlate the high-low inversion in quartz with the ferromagnetic Curie points.[26] However, Perrier, with his associates, did not succeed in finding the sharp maximum in the dielectric constant which he had predicted.[27] It was shown above (Section VIII) that such an infinity point in the dielectric constant is to be expected at a transition from a pyroelectric to a nonpyroelectric crystal class. Quartz however is not truly pyroelectric on either side of its inversion point.

In recent literature there is, however, one new example for an infinity point of a dielectric constant: the transition of HBr at $-183°C$.[28] In the light of the present discussion it can be concluded that in this case a transition from a pyroelectric to a nonpyroelectric crystal class occurs.

XIII. SYMMETRY OF FERROMAGNETIC CRYSTALS

It is possible to extend the crystallographic argument of this paper to the ferromagnetic crystals themselves and to postulate that, e.g., an iron single crystal is a pseudocubic crystal; and that the real crystal individuals are the Weiss regions, which have, in absence of an applied magnetic field, a spontaneous polarization in the direction of one of the cube edges and are therefore *tetragonal paramorphic*, C_4^h.[29] Owing to magnetostriction, the geometrical forms will also be of this lower symmetry.

This point of view seems correct, but hardly fertile, because: (1) the moment of spontaneous magnetization can easily be rotated away from the axis of easiest magnetization; (2) the molecular *magnetic* moments are only slightly coupled with the forces which determine the configuration of the crystal, of which the most important are the *electrostatic* forces. This is entirely different for the case of spontaneous *electric* polarization in Rochelle salt.

The writer wishes to thank Professor W. G. Cady for his most valuable help in the preparation of this paper.

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[24] Sosman (reference 12), p. 334f.

[25] R. H. Fowler, Proc. Roy. Soc. **A149**, 1; **151**, 1 (1935).

[26] A. Perrier, Arch. sci. phys. nat. (Geneva) (4) **41**, 492 (1916).

[27] S. Gagnebin, Arch. sci. phys. nat. (Geneva) (5) **6**, 161 (1924).

[28] C. P. Smyth and C. S. Hitchcock, J. Am. Chem. Soc. **55**, 1830 (1933).

[29] In this classification it is taken into account that the magnetic polarization is an *axial* vector.