ON THE NATURE OF TWINNING IN POTASSIUM AND RUBIDIUM DITHIONATES

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Introduction

As mentioned in a previous communication,[1] a paper by Hägg[2] on the structure of potassium and rubidium dithionates (trigonal trapezohedral class, space group D_3^2)is of particular interest because it is probable that his crystal of rubidium dithionate was twinned. In connection with the Laue diagrams which he obtained from the two dithionates, Hägg[2] says "Bezüglich der Symmetrie der Lauephotogramme ist es bemerkenswert, dass während die Photogramme von $K_2S_2O_6$ die Lauesymmetrie D_{3d} deutlich zeigen, die Photogramme von $Rb_2S_2O_6$ beinahe die Lauesymmetrie D_{6h} besitzen." Regarding photographs taken with the beam along the *c* and *a* axes, respectively, of crystals of $K_2S_2O_6$ and of $Rb_2S_2O_6$, "dort sieht man wie bei $Rb_2S_2O_6$ eine Symmetrie niedriger als D_{6h} nur im Photogramme entlang der zweizähligen Achse, aber nicht mehr im Photogramme entlang der trigonalen Achse wahrgenommen werden kann." Furthermore, a detailed examination of Hägg's Fig. 1*d* (beam along an *a*-diad-axis) shows that the lower (D_3^d) symmetry is exhibited only if the relative intensities of equivalent spots are considered. From the point of view of geometrical position only, the symmetry appears to be that of D_6^h (*cf.* Fig. 1*D* of our previous note).[1]

Hägg was aware of the possibility of twin formation because he states that, "Die Lösungen wurden bei 85° abgedampft um die Zwill'ngsbildung zu vermeiden, die nach Fock unterhalb etwa 70° sehr ausgeprägt wird." Fock[3] apparently was able to obtain trigonal specimens by evaporation between 70°C. and 80°C. whereas at lower temperatures only hexagonal crystals were observed. It may be mentioned that Wyrouboff,[4] who cites Fock's work, claims to have been unable to obtain trigonal crystals.

Hägg[2] suggests two alternative explanations for his observations that, although crystals of $K_2S_2O_6$ clearly show the Laue symmetry of D_3^d, the Laue symmetry of $Rb_2S_2O_6$ is "nearly" that of D_6^h. According to Hägg, "Entweder besitzt in beiden Salzen das Metallatomgitter die Lauesymmetrie D_{6h}, die dann zu überwiegen beginnt wenn die Metallatome schwerer werden, oder der Übergang von Kalium- zu Rubi-

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[1] Barnes, W. H., and Wendling, A. V., *Am. Mineral.*, vol. **20**, pp. 253–259, 1935.
[2] Hägg, G., *Zeits. Krist.*, vol. **83**, pp. 265–273, 1932.
[3] Fock, A., *Zeits. Krist.*, vol. **6**, p. 161, 1881.
[4] Wyrouboff, M. G., *Ann. Chim. Phys.*, (6), vol. **8**, pp. 340–417, 1886.

diumatomen ist von einer Parameteränderung begleitet, die eine Annäherung an höhere Symmetrie verursacht."

Experience in this laboratory has been that the tendency to twin formation at ordinary temperatures is very much more pronounced in rubidium dithionate than it is in the potassium salt. During the determination of the space group of $K_2S_2O_6$, Helwig[5] encountered no crystals of that salt possessing pseudohexagonal Laue symmetry. However all crystals examined by Hankel and Lindenberg[6] in connection with studies of pyro- and piezoelectricity were Dauphiné law twins, although in some the twinned part was relatively small.

In preparing crystals of rubidium dithionate for a structure investigation to be described in due course, evaporation was allowed to proceed always at room temperature. Although most of the specimens showed pseudo-hexagonal Laue symmetry, a few were obtained clearly showing the Laue symmetry of D_3^d, both with respect to the relative intensities of equivalent spots on the photographs and to their geometrical arrangement around the spot due to the undiffracted beam. The proportion of such trigonal crystals as compared with those giving pseudohexagonal photographs, similar to Hägg's reproductions, appeared to increase with the number of recrystallizations. Attempts to prepare twinned crystals of $K_2S_2O_6$, on the other hand, led to the identification of only one specimen showing pseudo-hexagonal Laue symmetry.

This experience tends to invalidate Hägg's tacit assumption that his crystal of $Rb_2S_2O_6$ was not twinned because it was grown at a certain temperature.

LAUE DIAGRAMS

Laue photographs were taken of trigonal and of pseudo-hexagonal crystals of $K_2S_2O_6$ and of $Rb_2S_2O_6$ with the beam along *a*, *b* and *c* axes, respectively, in each case. Simple visual inspection showed that the Laue symmetry exhibited by the trigonal crystals of both salts was D_3^d while that of the pseudo-hexagonal specimens was D_6^h if geometrical positions and *not* relative intensities of apparently equivalent spots were examined.[1] This conclusion was confirmed by gnomonic projection analyses, the results of which are summarized in Table 1. In this table, p represents the number of planes and f the number of forms involved; P signifies spots present on photographs of the twins but absent from those of the single crystals; S and W indicate spots present on photographs of corresponding twins and single crystals, but of stronger in-

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[5] Helwig, G. V., Ph.D. *Thesis* (Physics), McGill University, Sept. **1931.**

[6] Hankel, W. G., and Lindenberg, H., *Abh. math-phys. Klasse, sächs. Akad. Wiss. Leipzig*, vol. **18,** p. 361, 1892; vol. **21,** p. 11, 1894; *Zeits. Krist.*, vol. **27,** p. 515, 1897.

tensity (*S*) and weaker intensity (*W*), respectively, on those of the twins. Spots of equal intensities on corresponding photographs of twins and single crystals, respectively, need not be considered. Only those planes with respect to which no doubt existed are included in the data of Table 1. The smaller number of planes recorded for $Rb_2S_2O_6$ is due primarily to experimental conditions. An interesting feature of the detailed results is that very few planes of the same indices are involved in corresponding data for $K_2S_2O_6$ and $Rb_2S_2O_6$.

TABLE 1

			$K_2S_2O_6$	$Rb_2S_2O_6$
P	*c*	*p*	66	11
		f	13	3
	a	*p*	12	8
		f	6	4
	b	*p*	14	23
		f	8	12
S	*c*	*p*	67	33
		f	20	4
	a	*p*	38	6
		f	24	3
	b	*p*	30	37
		f	18	19
W	*c*	*p*	23	30
		f	12	7
	a	*p*	7	20
		f	7	8
	b	*p*	46	17
		f	30	8

The spots on the Laue diagrams added by twinning are such as to make the *ac* and *ab* planes appear as planes of pseudo-symmetry. The *bc* plane appears as a plane of symmetry in the Laue diagrams of the single crystals (Laue symmetry, $D_3{}^d$) and in those of the twins. The twinned crystals may, therefore, be considered as derived from the single specimens by a simple rotation of 60° (or 180°) about the *c* axis.

The posssibility of twinning due to rotary-inversion (or the introduction of a centre of symmetry) is eliminated since in such a case the Laue diagrams of the twins would be indistinguishable from those of the single crystals. This follows from the fact that a plane $(HK.L)$ becomes $(\overline{HK}.L)$ by a simple rotation of 180°, and finally $(\overline{HK}.\overline{L})$ by a subsequent inversion. Due to the operation of Friedel's law, $(HK.L)$ and $(\overline{HK}.\overline{L})$ cannot be identified separately by x-ray methods of analysis. The introduction of a centre of symmetry is equivalent to the so-called Brazilian twinning law in which *ac* (or *bc*) becomes the twinning plane, when *b* (or *a*) is the diad axis.

Beyond the elimination of twinning due to a rotary-inversion (equivalent to the Brazilian law), the Laue method alone is powerless as is evident from the following argument.

LIMITATIONS OF THE LAUE METHOD

The most common types of twinning found in crystals of the trigonal trapezohedral class are represented in Fig. 1, where the stereographic projections of right- and left-handed crystals are designated *R* and *L*, respectively. *RR* and *LL* represent corresponding projections for complete penetration twins of two right- and two left-handed crystals,

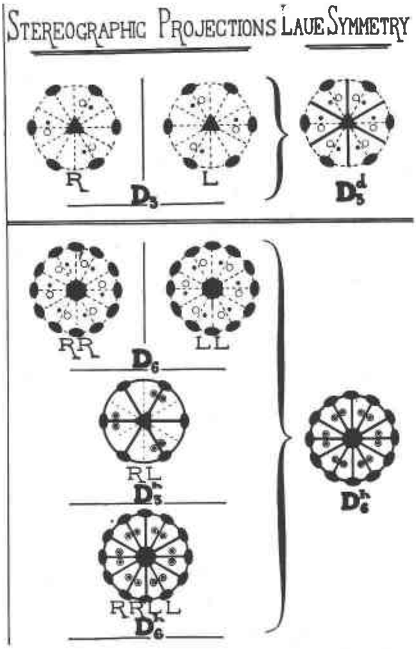

FIG. 1. Stereographic projections of possible twins in D_3.

respectively (Dauphiné law), and *RL* that for one right- and one left-handed crystal related to each other by reflection across the basal plane. The projection of the Brazilian type in which reflection occurs across the *ac* or *bc* planes, is not shown separately but is identical with that designated D_3^d in Fig. 1. Finally, *RRLL* represents the stereographic projection of complete hexagonal holohedral twinning and may be considered as due to a combination of two right- and two left-handed individuals, of *RR* and *LL*, or of two *RL* twins, respectively. The projections of *RR* and *LL* have the symmetry of D_6, that of *RL* has the symmetry of D_3^h while that of *RRLL* has the symmetry of D_6^h.

But, since the *x*-ray method automatically introduces a centre of symmetry, it is clear that, insofar as Laue symmetry is concerned, $R \equiv L \equiv D_3^d$, and $RR \equiv LL \equiv RL \equiv RRLL \equiv D_6^h$, the diagram of the latter class being derived from that of the former by a rotation of 60° (or 180°) and superposition on the original. The *x*-ray method alone, therefore, is unable to distinguish the four types of twinning represented in Fig. 1 one from another but does permit their differentiation from the Brazilian law. Furthermore, although there is no difference among the Laue diagrams of corresponding right and left crystals and a Brazilian twin, the last exhibits no or at least much reduced optical activity compared with the specific rotation of the single crystals.

Of the other four possible types of twinning, it is evident that measurements of optical activity may also be employed in their case to supplement the *x*-ray data and thus limit the possible types in any specific case. Thus for *RR* (and *LL*) the specific rotation will be the same as in *R* (and *L*), whereas for *RL* and *RRLL* the specific rotation will be less, and may be zero, depending on the relative proportions of the *R* and *L* constituents.

OPTICAL EXAMINATION

It has already been mentioned that only one pseudo-hexagonal specimen of $K_2S_2O_6$ has been found in this laboratory. Unfortunately it had been subjected to prolonged *x*-ray examination before the desirability of optical measurements was realized. Crystals of $K_2S_2O_6$ and of $Rb_2S_2O_6$ turn pink and then purple after extended exposure to *x*-radiation. In the case of the pseudo-hexagonal specimen of $K_2S_2O_6$ a pronounced purple tint was observed. Marked dichroism was manifested, the ordinary ray appearing colourless while the extraordinary ray was violet. Furthermore, this crystal possessed but one basal plane face and was too small to permit cutting the other. Finally, tabular fluid inclusions parallel to the basal plane were present. Under these circumstances, therefore, a study of the optical activity of this crystal could not be made.

According to Fock,[3] and Hankel and Lindenberg,[6] however, twins of $K_2S_2O_6$ are of the *RR* (or *LL*), *i.e.*, Dauphiné law, type.

As will be mentioned in a forthcoming paper on the structure of $Rb_2S_2O_6$, no optical activity could be detected in a pseudo-hexagonal crystal of $Rb_2S_2O_6$ whereas a trigonal crystal showed a specific rotation of about 2° per mm. Since the twin showed pseudo-D_6^h Laue symmetry (thus eliminating the Brazilian law), it follows that twinning in $Rb_2S_2O_6$ probably is of the *RL* or *RRLL* type. This conclusion receives some indirect confirmation from the fact that Topsøe and Christiansen[7] observed no optical activity in crystals of $Rb_2S_2O_6$ whereas Wyrouboff[4] reports very slight activity. It may be inferred, therefore, that these investigators examined twinned crystals composed of different relative proportions of *R* and *L* individuals.

Discussion

Although limitations of the Laue method prohibit identification of Brazilian twins from single individuals on the one hand, and distinction among the types of twinning designated *RR*, *LL*, *RL*, and *RRLL* in Fig. 1 on the other, there are occasions when a crystal suitable for Laue photographs but unsuitable for complete crystallographic examination will permit measurements of optical activity. On the basis of Laue photographs alone, Brazilian twins can be distinguished immediately from those due to the other types under discussion. Measurements of optical activity then enable a Brazilian twin to be distinguished from the single (right- or left-handed) individual. Of the other four types of twinning considered, a distinction can be made on the basis of optical activity measurements between *RR* (and *LL*) on the one hand, and *RL* and *RRLL* on the other. Even if single crystal specimens are not available for comparison, a careful examination of the relative intensities of geometrically equivalent spots on the Laue photographs of crystals showing pseudo-D_6^h Laue symmetry may enable the presence of twinning to be detected. Thus, the x-ray method coupled with studies of optical activity enables some progress to be made in the determination of the nature of twinning in certain cases where the more exact methods of formal crystallography cannot be applied in full.

It is of interest to note that Schubinkow and Zinserling[8] have employed Laue diagrams (obtained with the x-ray beam along the c axis)

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[7] Topsøe, H. and Christiansen, C., *Vidensk. Selsk. Skr. Kopenhagen*, vol. **9**, p. 661, 1873; *Ann. Chim. Phys.*, (5), vol. **1**, pp. 5–99, 1874; *Pogg. Ann.*, *Ergänzb.*, vol. **6**, pp. 499–585, 1874.

[8] Schubnikow, A., and Zinserling, K., *Zeits. Krist.*, vol. **83**, pp. 243–273, 1932.

in conjunction with optical studies to demonstrate that mechanical twinning in quartz, due to pressure, is of the Dauphiné (*RR* or *LL*) type. The twin gave a pseudo-hexagonal Laue diagram but the optical activity was the same as in the single crystal.

Specifically, the present study has identified a pseudo-hexagonal (twinned) crystal of $Rb_2S_2O_6$ as of the *RL* or of the *RRLL* type. In view of the statements of Fock[3] and of Hankel and Lindenberg[6] (*i.e.*, that twins of $K_2S_2O_6$ are of the *RR* or *LL* type), twinning in the isomorphous $K_2S_2O_6$ and $Rb_2S_2O_6$ apparently is according to different laws.

In view of the fact that we have obtained Laue photographs of $K_2S_2O_6$ and of $Rb_2S_2O_6$ with the beam along *a*, *b* and *c* axes that in all cases show the symmetry to be expected, namely D_3^d, and that we have also obtained corresponding photographs of other specimens of both salts showing the symmetry of D_6^h with regard to relative geometrical positions (but, D_3^d with respect to relative intensities), there is no doubt that Hägg's crystal of $Rb_2S_2O_6$ was a twin.

Single individuals of neither $K_2S_2O_6$ nor of $Rb_2S_2O_6$ yield Laue diagrams that are good examples of those from typically trigonal crystals, such as α-quartz[9] or, particularly, tourmaline.[10] Furthermore, on casual inspection, the diagrams of $Rb_2S_2O_6$ are less obviously trigonal than are those of $K_2S_2O_6$. It is, therefore, of interest to examine the hypotheses of Hägg in this connection despite the fact that they were proposed to account for the observation that a crystal, which was expected to show the symmetry of D_3^d, in reality appeared to possess pseudo-D_6^h symmetry.

The alkali metal ions in $K_2S_2O_6$ and in $Rb_2S_2O_6$ occupy the special positions $(e)+(f)$ of D_3^2.[11] In view of Hägg's suggestion that the lattice of these ions may possess the symmetry of D_6^h, the space groups of those classes (D_3^h, C_6^v, D_6, D_6^h) having the Laue symmetry of D_6^h were examined to determine if these special positions (uuO; $O\bar{u}O$; $\bar{u}OO$; $u'u', \frac{1}{2}$; $O\bar{u}', \frac{1}{2}$; $\bar{u}'O, \frac{1}{2}$) are possible therein. Since u and u' may have any values independently of each other, $(f)+(g)$ of D_{3h}^3 is identical with $(e)+(f)$ of D_3^2. The alkali metal ions, therefore, *are* on a lattice possessing the Laue symmetry of D_6^h.

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[9] Barnes, W. H., and Wendling, A. V., *Trans. Roy. Soc.* (Canada), vol. **27**, Sect. 3, pp. 133–140, 1933.

[10] Barnes, W. H., and Wendling, A. V., *Trans. Roy. Soc.* (Canada), vol. **27**, Sect. 3, pp. 169–175, 1933.

[11] Symbols for crystal classes, space groups and special positions are those employed by Wyckoff, R. W. G., Analytical Expression of the Results of the Theory of Space Groups, *Carnegie Pub.* **318**, 2nd Ed., Washington, 1930.

The alternative suggestion of Hägg that an approach to higher symmetry may be due to changes in the parameters of the alkali metal ions may be discarded since in (*e*)+(*f*), the only variable parameters, may have any values independently of each other without affecting the holohedral Laue symmetry of their lattice.

It is probable, therefore, that Hägg's suggestion regarding the influence of the potassium and, notably, of the heavier rubidium ions on the Laue symmetry of the crystals as a whole may account for the fact that trigonal Laue diagrams of $Rb_2S_2O_6$ are less obviously trigonal than those of $K_2S_2O_6$, despite the fact that it was proposed to account for the Laue symmetry of crystals of $Rb_2S_2O_6$ that were assumed to be single crystals but, in view of the results of the present study, certainly were twins.