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*Crystallographic notes on Inosite, Potassium nitrate, and
Urea nitrate.*

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(1) INOSITE.

CRYSTALS of Inosite, $C_6H_6(OH)_6 \cdot 2H_2O$, were first measured by Cloëtta,¹ and somewhat later by Zepharovich,² and by Lewis;³ they are monoclinic, and the elements adopted are those of Zepharovich, viz., $a : b : c = 1.0872 : 1 : 1.5602$; $\beta = 111^\circ 39'$. The observed forms on the crystals were {010}, {110}, {100}, {001}, {101}, {214}, {210}, and {410}, and it is seen that the form-development is of a somewhat anomalous character, the indices of the last three forms being remarkable for their complexity.

Now the observation of forms with relatively high indices is not uncommon, but as a rule they do not rank among the principal forms, being of a subsidiary character and only developed on certain crystals. In inosite, however, the form {210} is as well developed as {110}; further, {214} is the only pyramidal form on the crystals, and, according to Cloëtta, is the predominant form. What is equally significant is the fact that simple forms like {111}, {111}, {101}, and {011} are not at all represented. These considerations led Fedorov⁴ to the conclusion that the directions hitherto chosen for the crystallographic axes in inosite

¹ A. Cloëtta, Liebig's Annalen d. Chem., 1856, vol. xcix, p. 291.

² V. v. Zepharovich, Sitzungsber. Akad. Wiss. Wien, 1868, vol. lviii, Abt. 2, p. 121.

³ W. J. Lewis, Phil. Mag., 1878, ser. 5, vol. v, p. 141; Proc. Cryst. Soc., 1882, pt. ii, p. 51; Zeits. Kryst. Min., 1878, vol. ii, p. 190.

⁴ E. S. Fedorov, Zeits. Kryst. Min., 1903, vol. xxxviii, p. 327.

do not represent the real principal directions in the crystal. The form-development on critical examination points to a hypohexagonal structure, and he therefore proposed a new setting, which is undoubtedly far more in accordance with the molecular structure, inasmuch as the forms thereby acquire simpler indices. When this new setting is adopted, however, there is a certain hiatus in the form-development, for two or three forms having simple indices have not been observed.

Professor Fedorov kindly suggested to the author that a variation of the conditions of crystallization might lead to the development of the expected forms. The crystals hitherto investigated were crystallized from a cold solution, so it was decided to study the crystallization at a higher temperature. A quantity of inosite was very courteously put at the author's disposal by Dr. Hugo Müller, and crystals were obtained by slowly cooling an aqueous solution which was saturated at about 60° C. The crystals were measured on the two-circle goniometer and two new forms having very simple indices were observed. The three forms with most complex indices previously observed were not at all developed, so that the form-development of the author's crystals is nearly ideal and confirms the correctness of Fedorov's setting in a very conclusive manner.

Adopting for the present the old setting, the forms observed by the author were: $b\{010\}$, $c\{001\}$, $q\{012\}$, $r\{101\}$, $s\{102\}$, and $p\{210\}$; the new forms are $q\{012\}$ and $s\{102\}$. The crystals were tabular parallel to $b\{010\}$, but the direction of elongation was the edge cb as is shown in fig. 1. The zone cb was therefore set up as the prism-zone on the goniometer, and the readings of ϕ and ρ obtained do not hold for a crystal as generally set up with the edge am vertical. The theoretical values of the angles for a crystal set up in the former way have been calculated from the elements of Zepharovich, and are given in the following table:

Face.	ϕ (Azimuth). ¹			ρ (Polar Distance).		
	Observed Limits.	Mean.	Calculated.	Observed Limits.	Mean.	Calculated.
$q\{012\}$	49° 40'—51° 52'	51° 10'	54° 3'	—	—	—
$s\{102\}$	89 35—90 0	89 54	90 0	42° 45'—44° 41'	43° 58'	47° 48'
$r\{101\}$	89 28—90 55	90 14	90 0	15 32—16 52	15 59	19 26
$p\{210\}$	321 11—323 14	322 20	323 51	38 51—35 58	34 59	35 57

¹ Face of origin, the plane of symmetry $b(010)$.

In some cases twinned crystals were observed with $c(001)$ as twin-plane, the forms developed being $\{010\}$, $\{012\}$, and $\{210\}$. Twinning on the same plane was previously observed by Zepharovich, but of course with a different form-combination.

It immediately follows from the large discrepancies between the mean observed and calculated values that the angles are not very trustworthy, and the material was re-crystallized many times in the hope of getting better developed crystals. The faces, with the exception of (010) which was used as a face of reference, were always rounded and the reflections on that account either very faint or, where they were bright, of a multiple character. Although so unsatisfactory, the readings are sufficiently

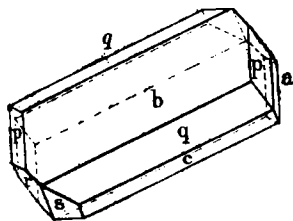


FIG. 1.—Crystal of Inosite.

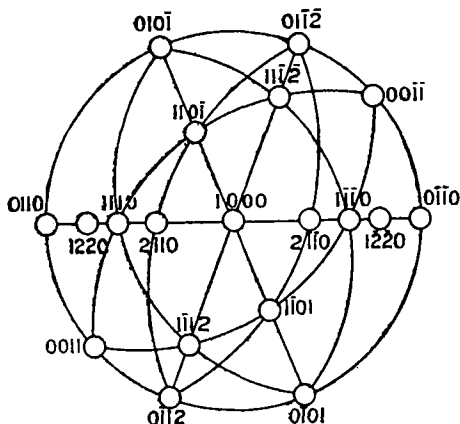


FIG. 2.—Stereographic projection, on the plane of symmetry, of the crystal-forms of Inosite. (The first index refers to the intercept on the dyad (hypohexagonal) axis of symmetry.)

good to determine the indices of the new faces ; moreover, the extinction on the face $b(010)$ with respect to the edges between it and the faces of the zone $[010]$ in all cases was in accordance with the optical determination of Zepharovich. A stereographic projection of all the forms hitherto observed is given in fig. 2. The cleavage is perfect parallel to $b(010)$.

In order to obtain the indices (q_0, q_1, q_2, q_3) in the hypohexagonal setting proposed by Fedorov from the indices (p_1, p_2, p_3) with the old setting of Zepharovich, the following transformation equations are made use of:

$$q_0 : q_1 : q_2 : q_3 = 2p_2 : p_1 + p_3 : p_1 : -p_3.$$

For example, in the case of the face $(\bar{2}14)$, $p_1 = \bar{2}$, $p_2 = 1$, $p_3 = 4$; inserting these values in the above equation we obtain—

$$\begin{aligned} q_0 : q_1 : q_2 : q_3 &= 2 \times 1 : \bar{2} + 4 : \bar{2} : \bar{4} = 2 : 2 : \bar{2} : \bar{4} \\ &= 1 : 1 : 1 : \bar{2} = (11\bar{1}\bar{2}). \end{aligned}$$

It may be remarked that the first index q_0 refers to the principal direction in the crystal, namely the pseudo-hexagonal axis which coincides with the dyad axis of symmetry. The following are the indices according to the old and new settings for all the forms found by different observers, as well as the form $(\bar{2}1\bar{2}) = (1011)$ which has never been recorded:

Old setting:	(010)	(001)	(012)	(101)	(100)	($\bar{2}1\bar{2}$)
New setting:	(1000)	(0101)	(1101)	(0011)	(0110)	(1011)
Old setting:	(210)	(102)	(110)	(214)	(410).	
New setting:	(1110)	(0112)	(2110)	(1112)	(1220).	

The forms are arranged in order of reticular density in the new setting, beginning with the plane of symmetry, which has the highest reticular density. It is seen from the table that the two new forms (012) and (102) possess a comparatively high position in the series, so that the combination of forms observed by the author approximates very closely to the ideal combination (i.e. a combination exhibiting faces of maximum reticular density). All that is required to make the combination ideal is the presence of the form $(\bar{2}1\bar{2}) = (1011)$ which has never yet been observed. Moreover, it is seen that Fedorov's setting is in harmony with the existence of a good cleavage parallel to the plane of symmetry, for the particles are most densely packed in this plane. With the old setting, on the other hand, the cleavage would be expected to be parallel to (001), for this would be the plane of maximum reticular density.

(2) THE RHOMBOHEDRAL MODIFICATION OF POTASSIUM NITRATE, AND ITS GROWTH ON CALCITE.

Potassium nitrate crystallizes as a rule in orthorhombic crystals with a pronounced prismatic habit, but at higher temperatures the form is rhombohedral and isomorphous with that of sodium nitrate. The transition temperature has been variously determined by different observers and appears to be about 128° C. It was observed by Frankenheim that the rhombohedral modification sometimes appears from aqueous solutions at the ordinary temperature; this is very unstable and more or less rapidly passes into the stable orthorhombic form.

The author has, from time to time, endeavoured to obtain the rhombohedral form from crystallizing drops of solution with a view to determining whether it is capable of forming parallel growths on calcite. The unknown conditions for its appearance would seem to be difficult to obtain, for the most varied trials with different samples repeatedly failed to give the wished-for results. A solution was at last obtained which deposited rhombohedral crystals; qualitative analysis of the salt failed to point to the presence of any impurity—as, for example, sodium nitrate—which might conceivably be the cause of the appearance of the rhombohedral modification.

The rhombohedra which crystallize from drops of the solution are clear and very well defined. They are microscopically, both with regard to their optical and geometrical characters, indistinguishable from crystals of sodium nitrate. The birefringence is very strong and the rhombohedron angle has, according to Frankenheim, the value $73^{\circ} 24'$, which is very close to the value ($73^{\circ} 37'$) for sodium nitrate.

After the growth of the rhombohedra has gone on for a little time, they rapidly lose their transparency and pass into a crystalline aggregate of the stable orthorhombic modification: the change is probably always brought about by contact with a small orthorhombic crystal, but the latter is in many cases so small as to be invigible. The belief that the change is actually brought about by nuclei of the stable modification is supported by the observation that the transformation of all the rhombohedra is not effected simultaneously, but goes on through the drop in a progressive manner at short intervals.

Attempts were made to obtain parallel growths on calcite by allowing drops of the saturated solution to crystallize on a fresh cleavage surface. The rhombohedra never failed to make their appearance, but no definite orientation was traceable: the edges of the rhombohedra were as a rule inclined at various angles to the edge of the calcite. After standing for some time, the transformation took place into the stable modification.

It may, therefore, be concluded that the rhombohedral modification of potassium nitrate is incapable of forming a parallel growth on calcite. Unfortunately, it has not been found possible to determine the specific gravity of this modification, owing to its instability, and the molecular volume therefore remains unknown. The author's previous work on isomorphous series, however, enables one to predict that the molecular volume should be about six units higher than that of sodium nitrate, which itself is slightly higher than that for calcite. The molecular volume, then, of rhombohedral potassium nitrate and calcite must show

a considerable difference, and on this account the experimental results were not wholly unexpected.

(3) UREA NITRATE, AND ITS OPTICAL BEHAVIOUR IN CRYSTALLIZING DROPS.

This substance ($\text{CO}(\text{NH}_2)_2 \cdot \text{NO}_3\text{H}$) has been the subject of repeated investigation. The crystals, which are really monoclinic, are almost invariably twins; this explains why Marignac,¹ who was the first to measure the substance, came to the conclusion that it is orthorhombic. A little later von Lang² expressed the opinion that the crystals might be monoclinic; and he determined the optical axial plane to be the plane of symmetry and the first positive mean line to be practically perpendicular to what was taken to be the basal plane, so that optically

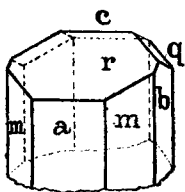


FIG. 3.—Simple crystal of Urea nitrate.

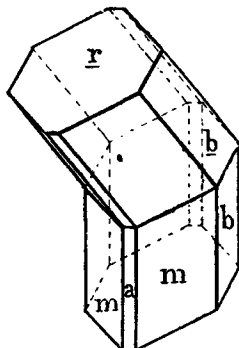


FIG. 4.—Twinned crystal of Urea nitrate. (Twin-plane $r(101)$.)

too the crystals simulate orthorhombic symmetry. Gaubert³ showed that the crystals are really twins on the basal plane.

It might be said that urea nitrate has already been sufficiently well investigated, but all the above observers failed to obtain any other forms except those lying in the prism-zone and the form (101), hitherto always held to be the basal plane, so that it was not possible to determine the ratio of the axes $c:b$. After many fruitless endeavours, the author succeeded in obtaining a crop of crystals which exhibited two new forms— $c(001)$ and $q(011)$. The former is taken to be the new basal plane, the old basal plane becoming (101).

¹ J. C. G. de Marignac, *Mém. Soc. Phys. Genève*, 1855, vol. xiv, p. 284.

² V. von Lang, *Sitzungsber. Akad. Wiss. Wien*, 1862, vol. xlv, p. 118.

³ P. Gaubert, *Compt. Rend. Acad. Sci. Paris*, 1907, vol. cxlv, p. 378.

The crystals were obtained by slowly cooling an aqueous solution. They are very soft and flexible, so that great care has to be taken in drying the crystals.

System: Monoclinic.

Ratios of the Axes: $a:b:c = 0.9965:1:0.9142$; $\beta = 75^\circ 2\frac{1}{2}'$.

Forms: $r\{101\}$, $b\{010\}$, $m\{110\}$, $c\{001\}$, $a\{100\}$, $q\{011\}$.

A typical crystal showing the new forms $c\{001\}$ and $q\{011\}$ is shown in fig. 3; these crystals were mostly untwinned. All the other crops examined were twins of the usual type with $r(101)$ as twin-plane (fig. 4). It may be observed that it is difficult to say without actual measurement on the goniometer whether a given crystal is a twin or is a single crystal with the two new forms, since on reflection across the twin-plane (101) the faces (100) and (110) approximately come into the position of the forms (001) and (011) on an untwinned crystal. It is therefore possible that crystals having the forms (001) and (011) have been previously obtained by other observers, but have been regarded as due to twinning.

The following are the results of the measurements obtained on the two-circle goniometer:

Face.	No.	ϕ (Azimuth).			ρ (Polar Distance).		
		Observed Limits.	Mean.	Calculated.	Observed Limits.	Mean.	Calculated.
$m(110)$	8	46° 1' — 46° 9'	*46° 5'	—	—	—	—
$a(100)$	2	—	90 0	90° 0'	—	—	—
$r(101)$	2	89 47 — 90 14	90 1	90 0	—	—	*84° 18'
$c(001)$	2	269 47 — 270 14	270 1	270 0	14° 57' — 14° 58'	*14 57½	—
$q(011)$	3	342 56 — 343 30	343 18	343 42	43 12 — 43 48	43 33	43° 36'

A control reading was taken of the angle (101): (011):

Found 60° 34', Calculated 60° 43'.

In order to transform the above setting into the one suggested by Fedorov, the following transformation equation must be used: $q_1:q_2:q_3 = p_2:-p_1:p_3$. Cleavage: $r(101)$ perfect. Optics (von Lang): Birefringence, negative; axial plane, (010); acute bisectrix perpendicular to $r(101)$; $2E = 21^\circ 10'$ (red), $23^\circ 10'$ (yellow), $24^\circ 30'$ (green), and $26^\circ 30'$ (blue).

Optical Behaviour in Crystallizing Drops of Urea Nitrate.

Well-defined, microscopic crystals of urea nitrate are obtained by placing a drop of warm, saturated aqueous solution on a microscope-slide, and the optical properties are of such a nature as to make the substance most useful for demonstration purposes. The crystals are practically always reflection-twins on $r(101)$, and they always lie either on the twin-plane or on the plane of symmetry. Since the optical properties of the crystals as viewed in these two positions are wholly dissimilar, it will be convenient to treat the two cases quite separately.

(1) *Crystals resting on the plane of symmetry $b(010)$.*—In this position the twinning is immediately evident by the re-entrant angles. Generally the crystals are contact-twins with (101) as both twin- and composition-plane (fig. 5 *a*); sometimes, however, interpenetration-twins occur (fig. 5 *b*), and occasionally the twinning is further repeated. Since the acute bisectrix is normal to the twin-plane $r(101)$, the two parts of the twin extinguish simultaneously, namely when the trace of the twin-plane is parallel to the plane of vibration of either nicol, that is, to either of the cross-wires in the eye-piece of the usual microscope.

On rotating the crystal and viewing with the polarizer without the analyser, the crystal experiences a remarkable change of relief; when the trace of the twin-plane is parallel to the vertical cross-wire (i. e. when the crystal is in the position of fig. 5 *a*) the relief is so low that it is very difficult indeed to make out the crystal outlines, whilst in the position perpendicular to this, the relief is at a maximum and is extremely high. On rotating through 360° there are two positions of minimum and two of maximum relief. The profound change of relief is only noticeable while the crystal is immersed in the drop of concentrated solution; when the drop has dried up, the outlines of the crystal no longer vary in sharpness on rotation. It is evident that in the position of low relief (which coincides with a position of extinction under crossed nicols) the refractive index of the solution must be of about the same value as that of the ray traversing the crystal. According to von Lang's determination, the latter is the ray of minimum refractive index α . On rotating the crystal through 90° the ray traversing the crystal now has the value γ , which is much greater than α , and the crystal on this account stands out in bold relief.

(2) *Crystals resting on the twin-plane $r(101)$.*—In this case it is not possible to recognize the twins either geometrically or optically, for no re-entrant angles are visible, and, moreover, since the acute bisectrix

is perpendicular to the twin-plane, the twinned crystal behaves optically as a single crystal. The appearance of such a twin is shown in fig. 5 c. The crystals extinguish uniformly parallel and perpendicular to the edge rb . In convergent light the characteristic biaxial interference-figure is visible: provided a sufficiently thin crystal be taken, the figure is as clear as in a prepared and mounted section and the optical characters can be easily made out.

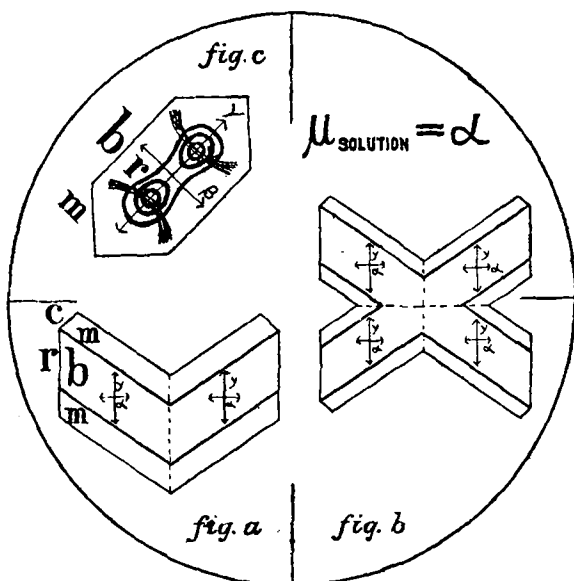


FIG. 5.—Growing crystals of Urea nitrate as seen under the microscope; showing a variation in optical character when viewed in different directions.

On examination with the polarizer there is no marked change on rotation, the crystal permanently remaining in high relief. This is what would be expected, for the two rays which traverse the crystal are the principal rays, having respectively the indices of refraction β and γ (cf. fig. 5 c). Now since the optic axial angle is small and the birefringence is negative, it follows that the β index is very close in value to the index γ , and both β and γ differ greatly from α , the last being approximately the value of refractive index for the solution.

The accuracy of the foregoing observations with respect to the orientation of the microscopic crystals has been confirmed by taking large crystals, the orientation of which had been first determined by measure-

ment on the goniometer, and then observing them under the microscope both in air and also when immersed in a saturated aqueous solution.

SUMMARY OF RESULTS.

1. The re-investigation of inosite has led to the observation of a new and very simple form-combination which confirms the correctness of the setting proposed by Fedorov.

2. The rhombohedral modification of potassium nitrate fails to give a parallel growth on a fresh cleavage of calcite.

3. The crystallographic constants of urea nitrate have been fully determined. Growing crystals of this substance under the microscope afford good illustrations of change of relief, twinning, and a very clear biaxial interference-figure.
