

Citation:

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the same for S_{u_1} , viz. $(G''_u + S_{u_1})$, then the metastable unary melting point of S_{u_2} , $(S'_{u_2} + L'_u)$, the corresponding point for S_{u_1} , $(S'_{u_1} + L''_u)$, and finally at a still higher pressure the unary transition point, $(S''_{u_2} + S''_{u_1})$.

OBSERVATION.

As is known it often occurs that though the vapour tension curves of two different modifications do not intersect below their melting point temperatures, the melting point curves of these two states do yield a point of intersection. In this case the system is *monotropic under the vapour pressure, but enantiotropic under the melting pressure*. As it is illogical to apply the terms monotropic and enantiotropic only to the case that the substance is under the vapour pressure, it is expedient to state when mentioning these phenomena, under what circumstances the system is considered to be. And just as we can now speak of monotropic and enantiotropic for a system that is under constant pressure, the same denominations can also be applied when the temperature is thought to be constant, as this has, moreover, been repeatedly done in this communication.

Anorg. Chem. Labor. of the University.

Amsterdam, Jan. 19, 1916.

Physics. — “*The Symmetry of the Rontgen-patterns of Tetragonal Crystals*”. By Prof. H. HAGA and Prof. F. M. JAEGER.

(Communicated in the meeting of February 26, 1916).

§ 1. For the purpose of further completing our experiments on the specific symmetry of the diffraction-images, which can be obtained by radiating through crystals by means of RONTGEN-rays, we publish in the following paper the results, which were obtained by us in the study of *tetragonal* crystals.

It appeared to be rather difficult to study an object of all seven classes of the tetragonal system, while many of the hitherto known representations of the mentioned symmetry-classes could hardly be obtained in such a degree of perfection, as is required for this kind of experiments. Moreover, from the tetragonal-bisphenoidical class no representatives are hitherto known,¹⁾ with certainty.

¹⁾ It is not yet certain, whether the compound $2CaO \cdot Al_2O_3 \cdot SiO_2$, mentioned by WEYBERG (Anz. d. Akad. d. Wiss. in Krakau, 611–616) (1906), may indeed be considered to be a representative of this symmetry-class.

Finally we were obliged to limit our study to the following crystal-species: *Rutile*; *Cassiterite*; *i-Erythrite*; *Scheelite*; *Nickelsulphate* ($6 H_2O$); *Nickelselenate* ($6 H_2O$); *Potassiumdihydrophosphate*; *Penta-erythrite*; and *Wulfenite*.

§ 2. The symmetry of the RONTGENpatterns for definite sections of tetragonal crystals of different classes has been already deduced by us ¹⁾, and the results reviewed. We can therefore refer here to them, and begin without delay with discussing the different crystal-species studied by us.

I. *Ditetragonal-bipyramidal Class.*

a. *Rutile*: TiO_2 , with axial ratio: $a : c = 1 : 0.6442$, our crystals originated from *Raade* in *Norway*. They were only imperfectly translucent as well as the sections of them, and full of very fine cracks. The obtained RONTGENpatterns were not very beautiful, and unsuitable for reproduction. Therefore only a stereographical projection is reproduced here (fig. 1 on Plate IV) of the image obtained in radiating through a crystal-plate parallel to (001); its thickness was 1.50 mm. The pattern evidently shows a quaternary axis, and four vertical planes of symmetry passing through it.

b. Better results were obtained with *Cassiterite*: SnO_2 . Our crystals, whose parameters were: $a : c = 1 : 0.6724$, originated from *Schlaggenwald* in *Bohemia*. Of the resulting images of crystal-plates parallel to {001}, {100} and {110} only that parallel to {001}, (thickness of the plate: 0,20 mm.) appeared to be reproduceable (fig. 1 on Plate I); it possesses, as can be seen from its stereographical projection on Plate IV (fig. 2), also a quaternary axis and four vertical planes of symmetry. Of the images obtained with plates parallel to {100} and {110} ($d = 0,22$ and $0,23$ mm.) stereographical projections are reproduced in fig. 3 and 4 on Plate IV: they possess two perpendicular planes of symmetry and a binary axis perpendicular to the photographic plate, quite in concordance with the theoretical deductions.

II. *Ditetragonal-pyramidal Class.* Notwithstanding numerous tentatives we did not succeed in obtaining any other object of this class than *Penta-erythrite* in a suitable form. The crystals of *Silverfluoride* were too hygroscopic, those of *Iodo-succinimide* too small.

However we were able to get very beautiful, transparent crystals of *Penta-erythrite*: $C_6H_{12}O_4$ ($= C(CH_2OH)_4$), mpt: $253^\circ C$. This compound, which according to MARTIN ²⁾ must belong to this

¹⁾ HAGA and JAEGER, these Proceed. 18 543. (1915).

²⁾ MARTIN, N. Jahrb. f. Miner. Beil. Bd. 7. 18. (1891).

crystal-class ($a:c = 1:1,0236$), possesses a very perfect cleavability parallel to (001), which made it possible to prepare very beautiful, homogeneous plates parallel to (001), and of varied thickness; their accurate orientation could be controlled sufficiently in convergent polarized light. By means of faultless preparations of this kind, which had a thickness of respectively 0,34 and 1,30 mm., we obtained very good and agreeing RÖNTGENpatterns, of which one is reproduced in fig. 11 on Plate III, and as stereographical projection in fig. 17 on Plate IV.

From these images it can be seen with certainty, that the crystals certainly possess a quaternary principal axis, but not vertical planes of symmetry. It follows immediately from this, that *penta-erythrite* cannot belong to this symmetry-class, but that it is *tetragonal-bipyramidal*, just like *scheelite*, or, what is far more probable in respect to the hemimorphy found by MARTIN, that it belongs in the same symmetry-class as *wulfenite*, and thus must be considered to be *tetragonal-pyramidal*. In any case the compound can be no longer reckoned to be a representative of the ditetragonal-pyramidal class of this system.

III. Tetragonal-bipyramidal Class.

a. From a crystal of *i-Erythrite* plates parallel to {001} and {100} were cut with a thickness of 0,85 and 0,81 mm., and radiated through. The axial ratio of this compound, whose composition is: $C_4O_4H_{10}$, is: $a:c = 1:0,3762$. The obtained RÖNTGENpatterns were too feeble for reproduction; however their stereographical projections are reproduced in fig. 5 and 6 on Plate IV. From fig. 5 it appears, that the pattern of a basal section possesses only a single quaternary axis, but *no* planes of symmetry; while from fig. 6, which because of the very weak negative can be only considered as an approximation, it may be seen, that there is only a horizontal plane of symmetry present. This fact also is in full agreement with the conclusions drawn from the theoretical interpretation of the representative of this phenomenon.

b. Other results were obtained in the case of *Scheelite*: $CaWO_4$, whose axial ratio is: $a:c = 1:1,5359$, and which according to the development of its limiting planes must be considered also to belong to this to symmetry-class.

Originally we had at our disposition very beautiful plates, cut from a crystal, which evidently seemed to be a homogeneous, single individual; this *scheelite*-crystal originated from *Schlaggenwald* in *Bohemia*, while later crystal-plates of a crystal from *Schwarzenberg*, *Gelbe Birke*, *Erzgebirge* were also investigated. Already soon the

very beautiful Röntgen-pattern obtained by means of a section perpendicular to the principal axis ($d = 0,24$ mm.) appeared to possess not only a quaternary axis, but also four vertical planes of symmetry passing through it. Moreover, also the images of plates parallel to (100) and (110), which had a thickness of resp. 0,19 and 0,18 mm., showed the presence of two planes of symmetry perpendicular to each other, and a binary axis. The original photos are reproduced in figs. 2 and 3 on Plate I, while their stereographical projections are published in figs. 7, 8 and 9 on Plate IV. The mentioned phenomenon may be observed therein immediately as well as the great number of spots; not the slightest indication can be found pointing to a lower degree of symmetry of these images.

It is natural to give an analogous explanation of this abnormal behaviour in the same way, as formerly was given in the case of *quartz*, namely by supposing a *twin*-structure to be the cause of it. Indeed *scheelite* often shows a twin-formation, which could be the cause of this strange behaviour: not seldom *scheelite*-twins are found with parallel axial-systems, which may be considered to be penetration-twins with an apparent symmetry after four planes, passing through the vertical axis; the RÖNTGENOGRAMS of such a penetration-twin would indeed show the symmetry observed by us. But our crystals showed neither a striation of the pyramidal faces, nor the occurrence of angles, nor any further indication for the correctness of the supposition, that really such a penetration-twin is present here. Of course an optical investigation cannot decide the question here in any way.

We tried to find out also the normal case, by studying in the same way a number of *scheelite*-crystals of the best quality, and from all kinds of places: from *Traversella* in *Piemont*, from *Kammegg* in *Guttannen* (*Berner Oberland*), from *Schwarzenberg*, etc. In fig. 4 of Plate I we have again reproduced one of these photos, obtained with a plate parallel to (001), and 0,26 mm. thick, cut from a crystal of *Guttannen*. But also here there could be no doubt whatever about the fact, that the RÖNTGEN-patterns of *all* these *scheelite*-crystals showed quite the same phenomenon. The image e. g. of the crystals from *Traversella*, although not completely centrically orientated, showed clearly the presence of planes of symmetry.

We must therefore conclude from this, that even externally perfectly single individuals of *scheelite*, in reality must be polysynthetic intergrowths of right- and left-handed crystals. We do not see that another explanation of the observed phenomenon is possible in this case, if not after all one were inclined to doubt the essential correctness

of the now established general theoretical interpretation of the symmetry of the diffraction-phenomenon studied; and this will no longer be possible after all proofs, which were gathered hitherto in favour of its correctness. Moreover, — even then it would be hardly possible to understand, why the symmetry of these RÖNTGEN-patterns appears to be so remarkably *high*. Thus we are for the present rather strongly compelled to accept the supposition of a polysynthetic twin-structure of all *scheelite*-individuals.

IV. *Tetragonal-trapezohedral Class.*

a. *Nickelselenate*: $NiSeO_4 + 6H_2O$. This compound was prepared from pure, cobaltfree colloidal nickeloxide, by solving it with an aqueous solution of pure selenic acid and evaporating the filtered solution in vacuo. The beautiful green crystals represent pyramidal crystals with the forms: {112}, {111}, {001}, {203}, {101} and {100}, and an axial ratio: $a : c = 1 : 1,8365$. The obtained RÖNTGEN-patterns are reproduced in figs. 6, 7, and 8 on Plate II, while in figs. 11 and 12 on Plate IV their stereographical projections are shown. The image obtained with a plate cut parallel to {001}, — this being 0,72 mm. thick, — possesses evidently a quaternary axis and four planes of symmetry passing through it, while the images parallel to {100} and {110}, ($a = 1,11$ mm. in both cases) manifest two planes of symmetry perpendicular to each other, their intersection thus being a binary axis. The higher symmetry of the three patterns is therefore also in this case in full agreement with the theoretical expectations.

b. Also to obtain a new case of Röntgenpatterns of isomorphously related substances, we investigated moreover the analogous *Nickelsulphate*: $NiSO_4 + 6H_2O$. At room-temperature we always obtained from aqueous solutions the rhombic-bisphenoïdical sulphate with $7H_2O$, whose Röntgen-pattern parallel to {001} appeared generally similar to the corresponding one of zinc-sulphate. Between 30° and 40° C. the tetragonal form is obtained, between 50° and 70° C., however, the monoclinic form of the hexahydrate, which monoclinic form e.g. in the case of the corresponding, isodimorphous cobalt-salt appears to be the more stable form even at ordinary temperatures. The tetragonal modification is deposited from solutions also at room-temperatures, if an excess of free sulphuric acid is added before ¹⁾. The crystals of $NiSO_4 + 6H_2O$ have an axial ratio: $a : c = 1 : 1,9061$; they are perfectly cleavable parallel to {001}.

¹⁾ It may be remarked here however, that in this case too, first monoclinic crystals are deposited, changing subsequently into the more stable tetragonal modification. Here thus the so-called rule of the reaction-steps (GAY LUSSAC, OSTWALD) is again illustrated in a rather striking way.

By means of such a cleavage-lamella, 1,65 mm. thick, we obtained a Röntgen-image, completely analogous to that of the corresponding selenate, and which only manifested another distribution of the intensities of the diffraction-spots; this last phenomenon will be discussed in the following paper more in detail.

The obtained photo is reproduced in fig. 5 on Plate II, and in stereographical projection in fig. 10 on Plate IV. The Röntgen-pattern possesses a quaternary principal axis, and four planes of symmetry intersecting at angles of 45° , — just as was theoretically expected.

c. Finally we investigated also a plate of *Strychnine-sulphate*: $(C_{21}H_{22}N_2O_2)_2 \cdot H_2SO_4 + 6H_2O$, cut perpendicular to the optical axis. This laevogyrotory substance, whose parameters are: $a:c = 1:3,312$, belongs to this symmetry-class too.

Indeed the pattern obtained with such a plate parallel to $\{001\}$, and 1,76 mm. thick, showed the aspect of the projection-figure 18 on Plate IV. Here also the quaternary axis and the four planes of symmetry passing through it, are immediately discernible. In connection with the relatively great ratio $a:c$, the principal spots appear crowded in a smaller distance from the central part of the figure.

On a former occasion we have mentioned already the very strongly dextro-, resp. laevogyrotory *Triethylenediamine-cobalti-bromide* ($+2H_2O$), which also crystallises in the tetragonal system, and which belongs either in this class, or in the bipyramidal one. In every case it can be seen from the approximative stereographical projection of the Röntgenpattern parallel (001) , which is reproduced once more in fig. 19 on Plate IV, that notwithstanding the strong rotatory power of the crystals, clearly four planes of symmetry can be discerned passing through the principal axis.

V. *Tetragonal-scalenohedrical Class.*

a. The only substance belonging to this class, which could be obtained in crystals suitable for our purpose, was *Potassium-dihydro-ortho-phosphate*: KH_2PO_4 , with the axial ratio: $a:c = 1:0,9391$. The Röntgenpatterns, which were obtained with crystal-plates parallel to (001) , (100) and (110) , ($d =$ resp. 1,20, 1,13 and 1,25 mm.), were so feeble, that with the exception of the image parallel to (110) (see fig. 9 on Plate III), they were unsuitable for direct reproduction. Therefore the corresponding stereographical projections are given in fig. 13, 14 and 15 on Plate IV. They prove, that the image parallel to (001) possesses a quaternary axis and four vertical planes of symmetry passing through it, while both the other patterns show a binary axis and two planes of symmetry perpendicular to

each other. Also in this case, therefore, the agreement between observed and expected symmetry appears to be beyond doubt.

VI. Tetragonal-pyramidal Class.

The only representative of this class at our disposal was *Wulfenite*: $PbMoO_4$; the results obtained with it are therefore reviewed here. The axial ratio of this mineral is: $a:c=1:1,5777$. The beautiful, orange-coloured crystals originated from *Yuma Co* in *Arizona*; later-on we investigated also yellow crystals of *Mammoth Mine* in the same country.

The Röntgen-pattern parallel to (001) ($d=0,24$ mm.) is reproduced in fig. 10 on Plate III, and as a stereographical projection in fig. 16 on Plate IV. Apparently, perhaps also really, this image shows an analogous increase of the theoretical symmetry, as was found in the case of *scheelite*. The images parallel to (100) and (110) also, although too feeble to be reproduced here as proof, make the presence of two planes of symmetry, perpendicular to each other, very probable. However, the innermost circles of spots show on the negative parallel to (001) a distribution of the intensities, as is indicated also in the corresponding stereographical projection, and which might prove that a lower symmetry yet manifests itself in this Röntgen-image, although only in a very feeble degree. In connection with the mentioned symmetry of the images parallel to (100) and (110) however, this supposed lower symmetry may appear still rather doubtful¹⁾. And in that case here again the question must arise, what the cause can be of this increase of the expected symmetry? Here too, a possible explanation of the fact could only be based upon the supposition of a twinning, which however in the case of *wulfenite* has been observed rarely or not at all. The not completely adjusted image of the crystal of *Mammoth Mine*, betrayed the presence of planes of symmetry also.

Of the *tetragonal-bisphenoidical class*, there are, as already mentioned no representatives known with certainty.

§ 3. If thus we review here the results obtained in this investigation, we can draw attention to the fact, that for six of the seven classes of the tetragonal system, a study of the degree of symmetry of the RÖNTGEN-diffraction-images was made; and that, with the exception of the cases of *scheelite*, and perhaps also of *wulfenite*, — which both show an abnormal increase of their degree

¹⁾ The particular shape of the spots in this case too makes it doubtful, if really no twin-structure plays a certain role here.

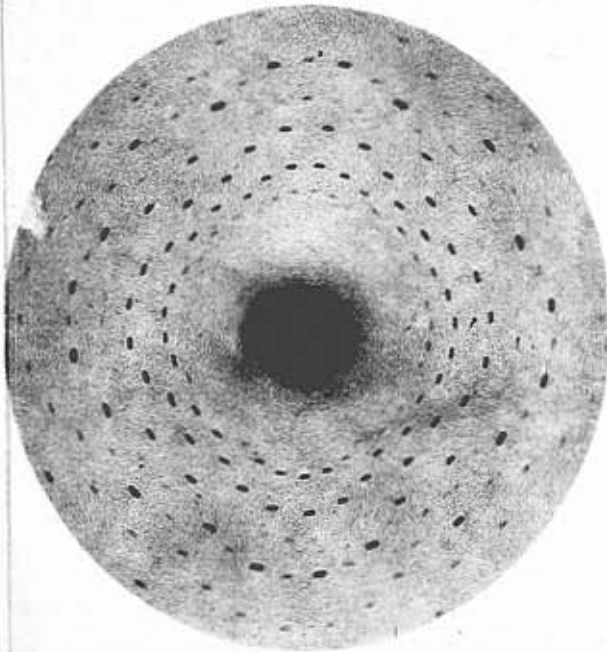


Fig. 1.
Cassiterite. Plate parallel to (001).

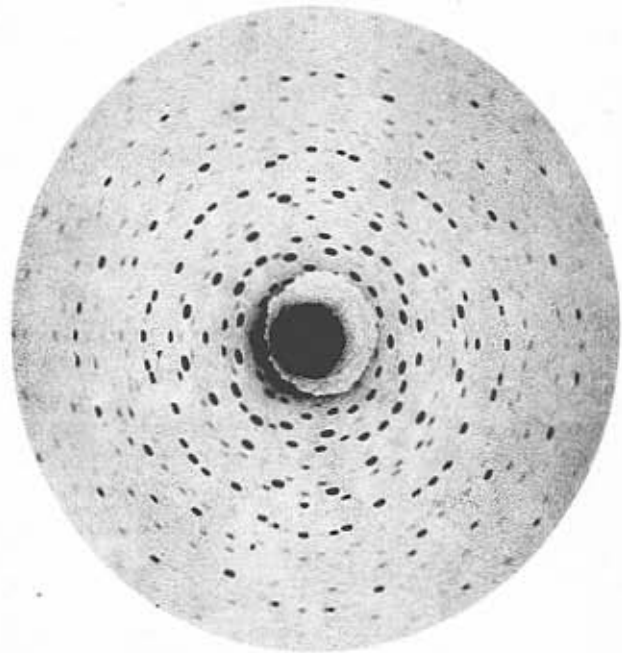


Fig. 2.
Scheelite. Plate parallel to (001).
(Schlaggenwald, Bohemen)

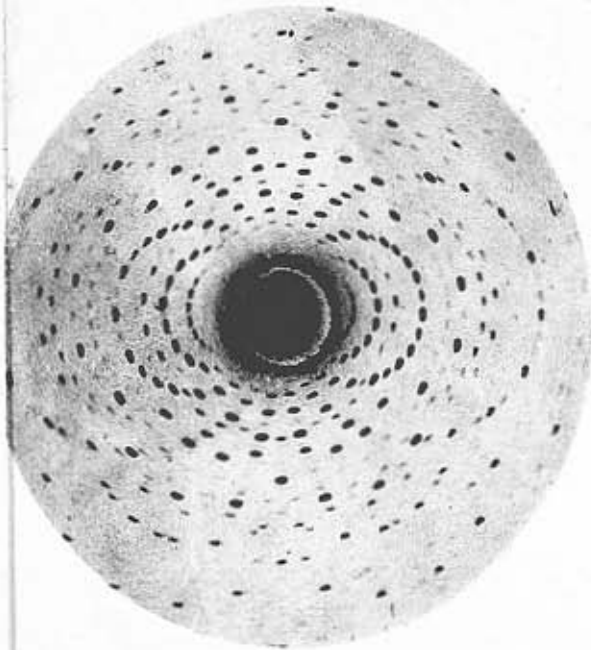


Fig. 3.
Scheelite. Plate parallel to (110).

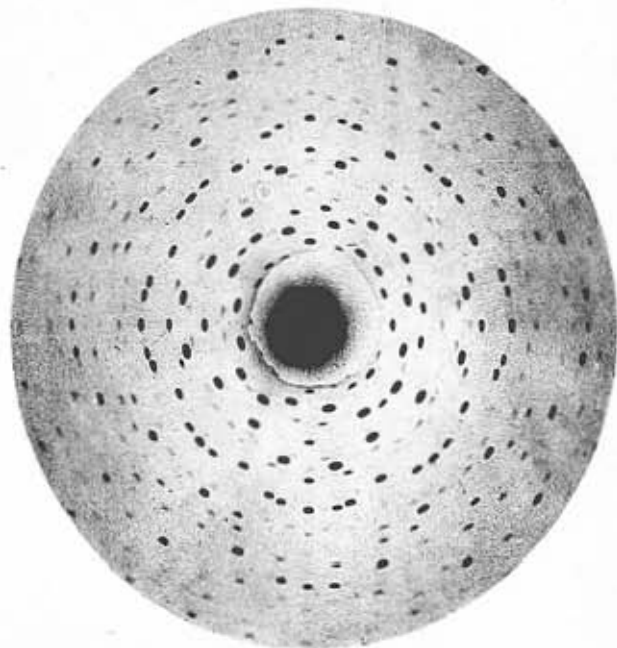


Fig. 4.
Scheelite. Plate parallel to (001).
(from Guttannen).

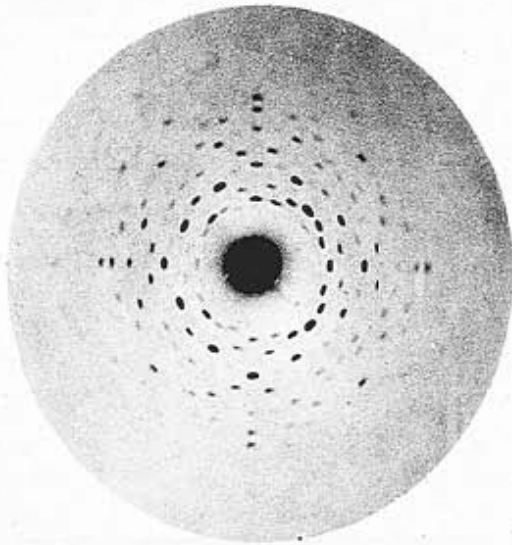


Fig. 5
Nickelsulphate. ($6H_2O$). Plate parallel to (001).

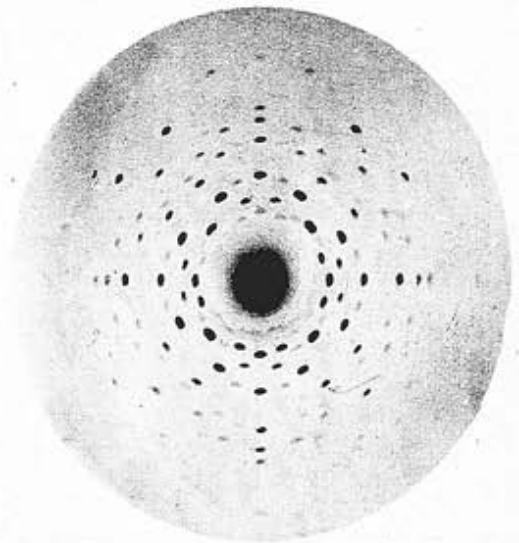


Fig. 6.
Nickelselenate ($6H_2O$). Plate parallel to (001).

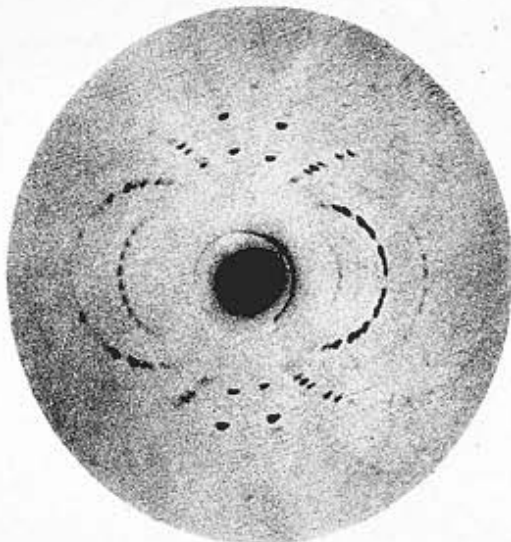


Fig. 7.
Nickelselenate. ($6H_2O$). Plate parallel to (100).

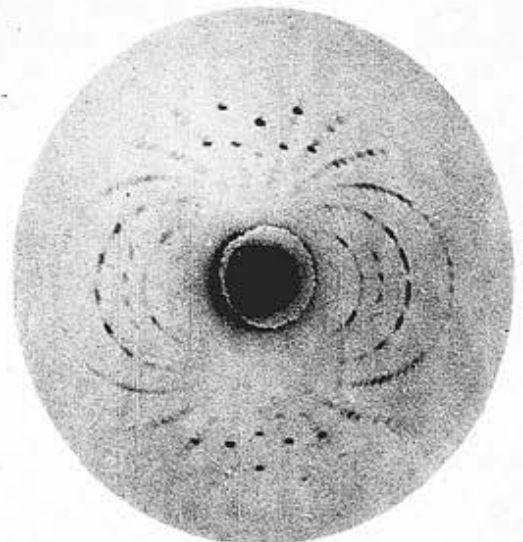


Fig. 8.
Nickelselenate. ($6H_2O$) Plate parallel to (110).

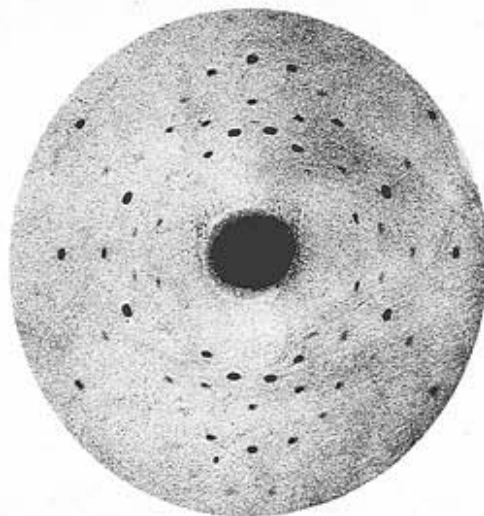


Fig. 9.
Potassiumdihydrophosphate. Plate parallel to (110).

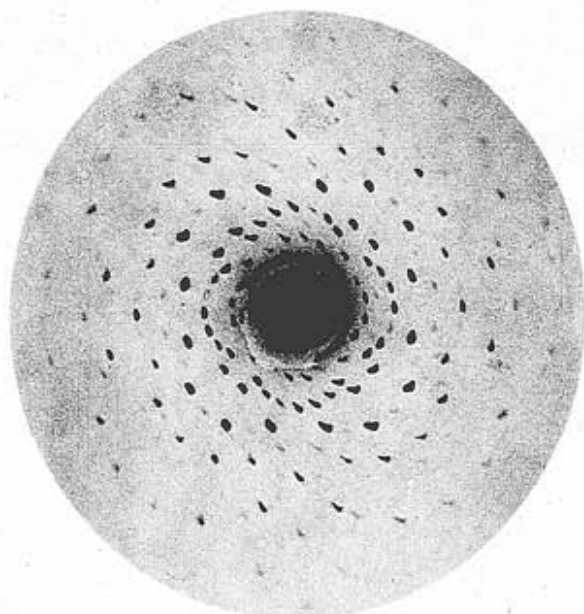


Fig. 10.
Wulfenite. Plate parallel to (001).

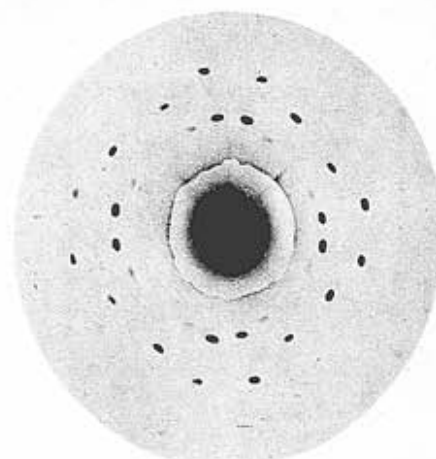


Fig. 11.
Penta-erythrite. Plate parallel to (001).

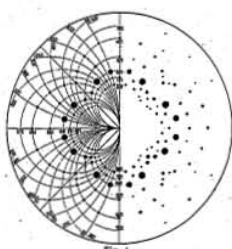


Fig. 1. Stereographical Projection of the Röntgen-pattern of Rutile. Plate parallel to (01).

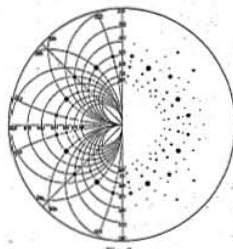


Fig. 2. Stereographical Projection of the Röntgen-pattern of Cassiterite. Plate parallel to (01).

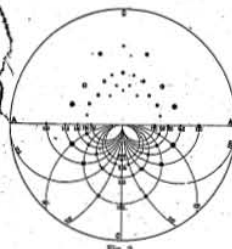


Fig. 3. Stereographical Projection of the Röntgen-pattern of Cassiterite. Plate parallel to (10).

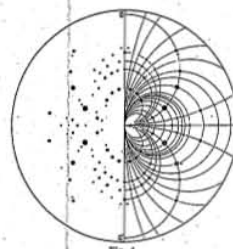


Fig. 4. Stereographical Projection of the Röntgen-pattern of Cassiterite. Plate parallel to (11).

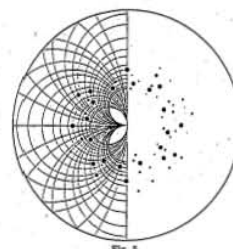


Fig. 5. Stereographical Projection of the Röntgen-pattern of inact. Erythrit. Plate parallel to (01).

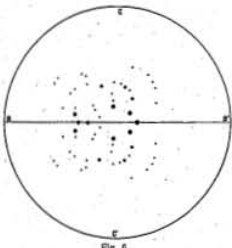


Fig. 6. Stereographical Projection of the Röntgen-pattern of act. Erythrit. Plate parallel to (10). (Schematic).

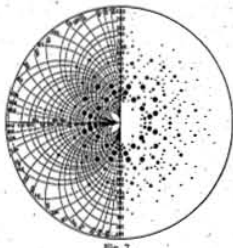


Fig. 7. Stereographical Projection of the Röntgen-pattern of Scheelite. Plate parallel to (01).

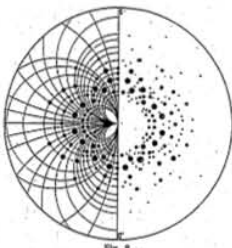


Fig. 8. Stereographical Projection of the Röntgen-pattern of Scheelite. Plate parallel to (01).

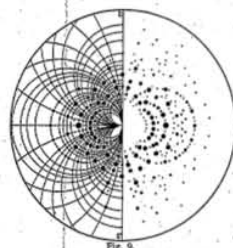


Fig. 9. Stereographical Projection of the Röntgen-pattern of Scheelite. Plate parallel to (11).

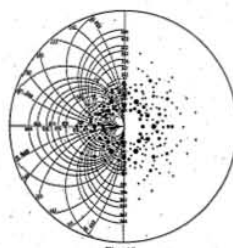


Fig. 10. Stereographical Projection of the Röntgen-pattern of Nickel-sulphate (NiSO₄). Plate parallel to (01).

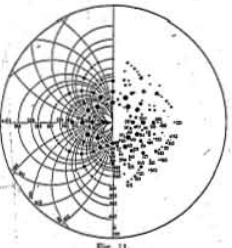


Fig. 11. Stereographical Projection of the Röntgen-pattern of Nickel-sulphate (NiSO₄). Plate parallel to (01).

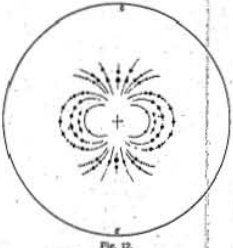


Fig. 12. Stereographical Projection of the Röntgen-pattern of Nickel-sulphate (NiSO₄). Plate parallel to (11).

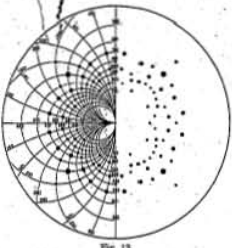


Fig. 13. Stereographical Projection of the Röntgen-pattern of Potassium-dihydrophosphate. Plate parallel to (01).

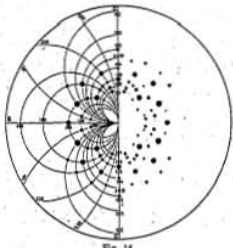


Fig. 14. Stereographical Projection of the Röntgen-pattern of Potassium-dihydrophosphate. Plate parallel to (10).

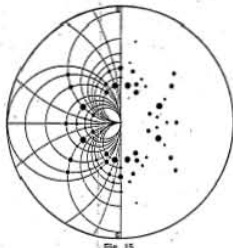


Fig. 15. Stereographical Projection of the Röntgen-pattern of Potassium-dihydrophosphate. Plate parallel to (11).

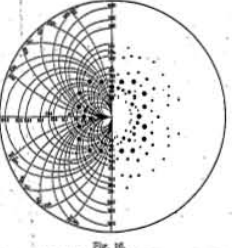


Fig. 16. Stereographical Projection of the Röntgen-pattern of Wulfenite. Plate parallel to (01).

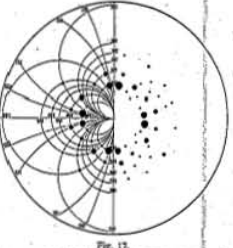


Fig. 17. Stereographical Projection of the Röntgen-pattern of Para-erythrit. Plate parallel to (01).

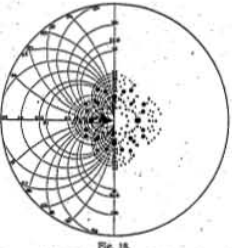


Fig. 18. Stereographical Projection of the Röntgen-pattern of Strychnine-sulphate. Plate parallel to (01).

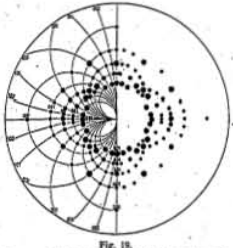


Fig. 19. Stereographical Projection of the Röntgen-pattern of dextro- and laevogyrate Trisilylene-diamino-Cobalto-bromide. Plate parallel to (01). (Approx.)

of symmetry probably by twinning, — we found in all cases an agreement between the actually observed and the theoretically predicted symmetry of the RONTGEN-patterns of these tetragonal crystals. The principal correctness of the diffraction-theory is thus proved here sufficiently for tetragonal crystals also.

Furthermore it could be shown, that *penta-erythrite* cannot be of ditetragonal-pyramidal symmetry, as hitherto assumed, but that it can probably be only tetragonal-pyramidal.

*Laboratories for Physics and for Inorganic
and Physical Chemistry of the University.*

Groningen, February 1916.

Mineralogy. — “*On Rontgen-patterns of Isomorphous Crystals.*”
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§ 1. In the following paper we wish to discuss the results, which were obtained by us in radiating through the similarly orientated planparallel plates cut from crystals, which are related to each other as direct “isomorphous” ones. To avoid unnecessary complications, we used for this purpose crystals of inorganic substances of relatively simple chemical composition, in whose analogously built molecules every time one single species of atoms was substituted by another closely related species. Thus in comparing one term of a series with another one, only one single of the structural elements is substituted by another one.

§ 2. The isomorphous compounds, whose Rontgen-patterns were compared with each other, were the following:

a. The series of the rhombic-bipyramidal, typically pseudo-hexagonal carbonates of calcium, strontium, barium and lead, which are found in nature as the minerals *arragonite*, *strontianite*, *witherite* and *cerussite*.

b. The carbonates of calcium and manganese, which are found as the ditrigonal-scalenohedral minerals *calcite* and *rhodochrosite*¹⁾ in beautiful crystals.

c. The series of the rhombic-bipyramidal sulphates of the metals calcium, strontium, barium and lead, which are known in mineralogy as the minerals *anhydrite*, *coelestine*, *baryte* and *anglesite*.

¹⁾ Or *diatagite*.