Citation:

Haga, H. & F.M.Jaeger, Röntgenpatterns of Boracite, obtained above and below its inversion-temperature, in:
KNAW, Proceedings, 16 II, 1913-1914, Amsterdam, 1914, pp. 792-799

Mineralogy. — *"Röntgenpatterns of Boracite, obtained above and below its inversion-temperature".* By Prof. H. Haga and Prof. F. M. Jaeger.

(Communicated in the meeting of January 31, 1914).

§ 1. Comparison of numerous photographic diffraction-patterns, obtained by the method of Laue, Knipping, and Friedrich, i.e. by the transmission of Röntgen-rays through planparallel crystalplates, has led with increasing evidence to the conviction, that the symmetry of those patterns agrees with that of the space-lattice, which presents itself as the very fundament of the molecular arrangement of the investigated crystal. On this assumption, the new method of research will be in future a very important manner to elucidate the question, if with polymorphic changes, and principally in cases of enantiotropic inversions in the neighbourhood of the critical inversion-temperature, a change of the molecular arrangement takes place, or if the cause of polymorphism must be attributed to a change only of the crystalmolecules themselves.

This problem seemed to us of high importance, especially in the case of those remarkable reversible inversions, which are found in a class of crystals, whose optical behaviour does *not* agree with the symmetry of their external form, of their cohesion, etc., or generally speaking: with their total crystallographic character; so that it has been a custom already from an early date, to discern these cases as those of "optically anomalous" crystals. Of this class of mimetic crystals the minerals *boracite*: $Mg_7B_{16}O_{30}Cl_2$, and *leucite*: $K_2Al_2Si_4O_{12}$ may, after the investigations of Mallard, Klein, etc., be considered to be typical representatives.

The boracite crystallizes in forms, which by no means can be discerned from real hexakistetraedrical ones; even by the most accurate goniometrical measurements it appeared to be impossible to find any deviation of the external form from those possessing the above mentioned symmetry. On the other hand, however, the optical investigations, and also those concerning the corrosion-phenomena, have shown with perfect evidence, that the crystals of boracite possess *no* regular symmetry in the common way; they must be considered as composed by a very complicated system of birefringent lamellae, which according to their optical properties, cannot have any higher symmetry than that of rhombic crystals; these lamellae have intergrown in such a way, that their conglomerate corresponds, with respect to its external form, very exactly with a true regular crystal. More particularly the individuals of boracite seem to represent

H. HAGA and F. M. JAEGER. Röntgen-Patterns of Boracite below and above its inversion-temperature.

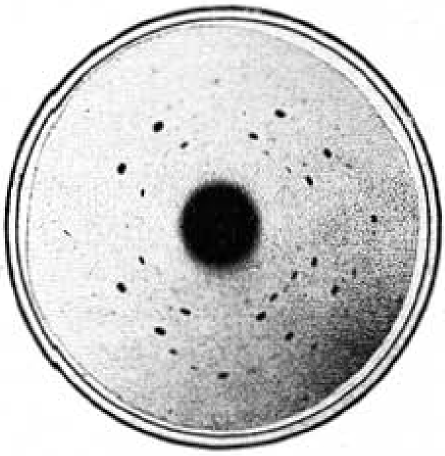


Fig 2.

Boracite 18° C. Distance: 42.5 mM.

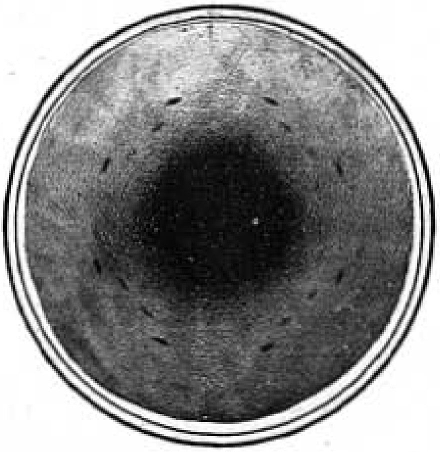


Fig. 3.

Boracite 300° C. Distance: 61 mM.

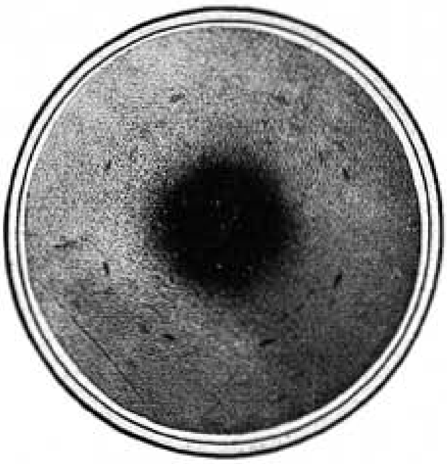


Fig. 4.

Boracite 18° C. Distance: 61 mM.

a polysynthetic twinformation of six hemimorphic rhombic crystals, whose twinning-planes are those of the apparent rhombendodecahedron. Normal to every plane of this form, the interference-image of a biaxial crystal can be observed in convergent polarised light, the plane of the optical axes being parallel to the longer diagonal of each face of the pseudo-rhombendodecahedron. At temperatures between 260° and 280° C., the boracite suddenly becomes optically isotropous; then it has got perfectly regular, and its optical properties are now in complete agreement with its external form. On cooling, the original birefringence returns as suddenly, as it has gone; the crystal represents afterwards again the case of an optically anomalous one.

These general considerations will be sufficient here for our purpose; therefore we will now begin the description of our experiments.

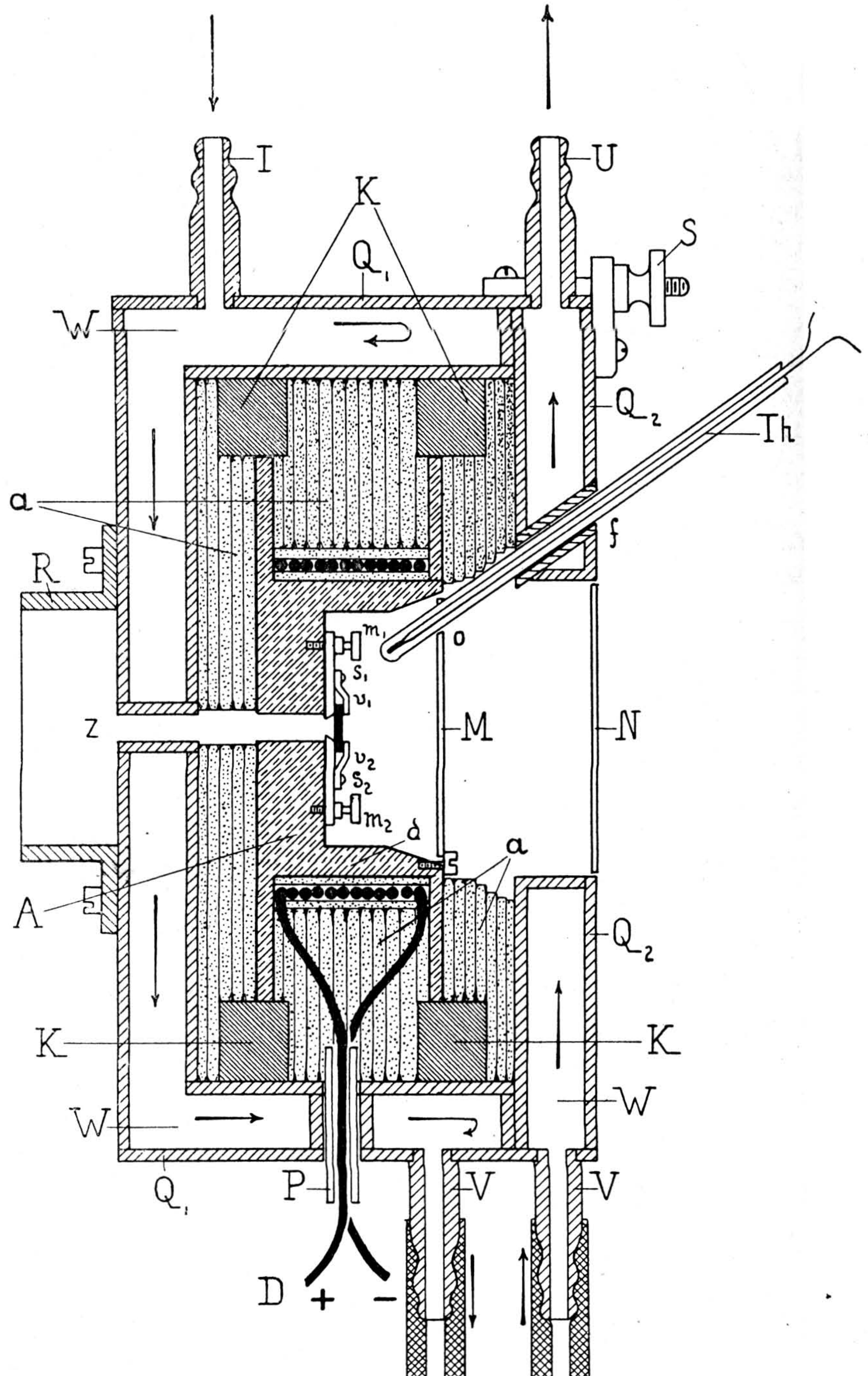
§ **2.** *The heating-apparatus.* To fulfil the condition, that the RÖNTGEN-rays might be transmitted as well at higher as at lower temperatures, a furnace of the form described here in detail, was constructed.

A box with double walls was made of polished brass; it incloses the whole furnace like a screen, and is kept at a constant temperature by means of a circulating stream of cold water. The hollow box is composed of two separate parts: one of them Q_1 bears a tube *R*, which can be connected with the RÖNTGEN-apparatus; further it has a cylindrical hole *z*, serving as a canal for the thin bundle of RÖNTGEN-rays. Cold water enters the box at *I*; after circulation it goes by *V* and *B* to the hollow cover Q_2, and leaves the apparatus at *U*. The cover Q_2 is fixed in position on Q_1 by means of three equidistant screws *S*. Q_2 possesses at *f* an oblique perforation, which serves for the adjustment of the thermoelement *Th*.

The heating-coil *D* consists of platinum-wire, 0,4 m.m. in diameter; it enters the furnace at *P*, where it is insulated from the brass box by means of a porcelain-tube, and leaves the apparatus in the same way by a second hole of this kind. The heating coil is wound round a core of copper *A*[1]), from which it is insulated by means of a thin layer of asbestos-paper; the coil needs to be applied only in a single layer. The metal core *A* is held in a central position by means of six pieces of carbon; all intervening space is filled up with disks of heavy asbestos, cut in suitable dimensions.

---

[1]) For higher temperatures it must be recommended, to prepare this central part of the furnace from nickel, or to coat it heavily with gold; for the highest temperatures (up to 1600 C°.), *alundum*-cores of the *Norton Company* in *Worcester* (Mass.) U. S. A., are an excellent material.



$\frac{4}{5}$ full size

Fig. 1.

The core A possesses a somewhat thinner wall at d, and is conical excavated on the lathe, as indicated in the figure 1, with the purpose to give the rather strongly deviating RÖNTGEN-rays an opportunity to reach the photographic plate without an interposing obstacle. The furnace-chamber must be kept at a constant temperature however; therefore it is necessary, to shut it at M, and like-wise the cover Q_2, to protect the photographic plate from heat-radiation, at N_1 by means of a thin plate of aluminium, which can be fixed or removed by means of a copper-ring. In this way the heat is sufficiently kept in the chamber, while the aluminium-screens do not interpose any appreciable obstacle in the way of the RÖNTGEN-rays. The aluminium screens have, at o, only a hole to introduce the thermoelement Th into the furnace. The crystal-plate p to be investigated, is fixed in position on a removable support, which can be adjusted in the furnace-chamber by means of the buttons m_1 and m_2, and a bayonet-joint under the screws s_1 and s_2, The crystal is fixed on the support by means of the two metal springs v_1 and v_2. The furnace-coil can bear a maximum current of 5,5 Ampères; with this intensity a temperature of 800° C. or somewhat higher, can be reached.

The connection of the furnace with the RÖNTGEN-apparatus was made in the following way. A brass plate was fixed in a vertical position on a long horizontal rail; against the vertical end of the plate a heavy lead-screen was fixed. In the brass plate a long brass tube of about 7 c.m. is fixed, and adjusted in a horizontal position; this tube bears at the side where the furnace stands, (i. e. at this side of the lead screen), a brass flange, which is turned off on the lathe in such a way, that the plane of its border is accurately adjusted perpendicularly to the direction of the emerging RÖNTGEN-rays. The tube R of the furnace just encircles the border of this flange. In the brass tube two cylinders of lead, about 5 m.m. long, are arranged at both terminals; they are fixed in such a way, that no rays can escape otherwise, than through the 1 m.m. broad central canals, which are pierced along the axes of the lead cylinders. As they are accurately adjusted so, that the axes of the two cylinders are lying in the same straight line, the direction of the bundle of RÖNTGEN-rays (about 1 m.m. in diameter) is wholly determined, as it were by means of a visor. Everywhere thick lead-plates are arranged so as to prevent the RÖNTGEN-ways from escaping otherwise, than through the narrow canal.

The furnace, with its axis in horizontal position, is now connected with the RÖNTGEN-apparatus, by pushing the tube R over the flange;

by a semi-cylindrical support, attached to the horizontal part of the brass plate, it is borne up from beneath, while a copperwire, wrapped round the double-walled cylinder of the furnace, helps to keep the apparatus in its position. It is necessary of course, to adjust the horizontal axis of the furnace exactly in the same level as the small canal for the emerging rays. The whole arrangement of the RÖNTGEN-tube, the lead screen, etc., corresponds principally with that described formerly by one of us.[1])

§ **3.** *The material.* The *boracite*, used in this investigation, was from Sehnde, in Hannover. It crystallized in clear, pale blue-green large crystals, showing the form {110}. Two planeparallel plates were cut from a crystal, one perpendicular to a binary, the other one perpendicular to a ternary axis of the apparent regular form.

Our experiments were only made with a plate, cut perpendicular to a binary axis; at the same time such a plate must be perpendicular to a quaternary axis of the BRAVAIS' space-lattice, if the crystal is really of the regular system.

By microscopic investigation the strong birefringence of the crystal-plate was easily demonstrated. It showed a typical polysynthetic structure; between crossed nicols it was in no position totally dark, but only locally. The composing lamellae showed high interference-colours; in convergent polarized light an interference-image of a biaxial crystal, almost perpendicular to an optical axis, was visible, with a dispersion, which would be in agreement with rhombic symmetry.

When the crystal-plate was heated in the microscope-furnace, already described by one of us, — in which furnace the crystal rests on the hot junction of the used thermoelement, — the polarisation-colours between crossed nicols change gradually from violet to yellow, blue and grey; then the field of the microscope gets dark *suddenly* at 266° C. On cooling the birefringence returns as *suddenly* as it disappeared; *it is an extremely remarkable fact, that almost the same lamellae return on that occasion, which were present already before heating.*

The experiment can be repeated arbitrarily; *thus we are quite sure, that in our experiments at fully* 300° *C. the optically isotropous form has always been present, while the birefringent one must have returned always after cooling to room-temperature.*

§ **4.** Our experiments now were made in such a way, that first a RÖNTGEN-photograph was taken, when the crystal-plate was out

---

[1]) H. HAGA, Ann. d. Physik (4). **23.** 439, 440. (1907).

of the furnace. Then the plate was fixed into the furnace, this was heated to fully 300° C. and left at this temperature during one hour; only after that time, the second photograph was taken. When the furnace had cooled down to room-temperature, a third photograph was taken, while the plate remained in the furnace and in the same position, as during the heating of it. The time of transmission of the RÖNTGEN-rays was 2 or 3 hours; this was shown to be sufficient, if a phosphorescent screen behind the photographic plate was used. The temperature of the furnace was under continuous control by means of the thermoelement *Th*. The obtained results were as follows.

Let us study first fig. 3[1]; it represents the image, obtained at 300° C. The crystal-plate was 1 m.m. thick, and was fixed at a distance of 61 m.m. from the photographic plate. Notwithstanding the fact, that the normal of the crystal-plate did not coincide absolutely with the normal on the face of the hexahedron, one can conclude from it, that the diffraction-pattern possesses a *quaterny* axis of symmetry, — just what might be expected in each of the three possible BRAVAIS' space-lattices of the regular system.

In fig. 4 the pattern is reproduced, obtained after the furnace has cooled down to room-temperature. The image is analogous to that of fig. 3 in a misleading way; however it doubtless differs from it. Especially the following facts may be brought more into the foreground: 1. in the quadrants to the right above and to the left below, in the first row of spots from the centre, there are found *three* small spots in close vicinity to each other; while at the same place in the opposite quadrants only *two* of these are present; 2. especially in fig. 2 it is very evident, that in both the rows, which are most elongated from the centre, there are only *five* spots between the two dark limiting ones, if the rows are situated at the opposite ends of a vertical diameter of the plate; but in the corresponding rows at the opposite ends of a horizontal diameter of the pattern, there are about *nine* spots between the two darker ones, while the spot in the midst of the row is darker than the others, and on both sides accompanied by a feebler spot. On the original negative of fig. 4 these differences could already be seen easily; but much better in the fig. 2, which represents the pattern obtained from a boracite-plate, 1,8 m.m. thick, but at a distance of only 42,5 m.m. from the photographic plate. Notwithstanding the fact, that this plate was not cut absolutely parallel to the face of the hexahedron; however, the

---

[1] We regret that the figures are only poor reproductions of the original röntgenograms, so that some details cannot be distinguished on them.

above mentioned differences can easily be stated. Another point of divergence of the figs. 3 and 4, which however does not relate immediately to the difference in period of the symmetry-axis, — is the fact, that in the fig. 4 (also in fig. 2), there are always two spots in the third row from the centre, which spots are missing wholly in fig. 3. We must conclude from this, that, notwithstanding the misleading analogy of figs. 2 and 4, with respect to fig. 3, the former two do not possess more than a *binary* axis of symmetry; with respect to the fact, that most observers contribute rhombic symmetry to the composing lamellae, it must be considered as highly probable, that this binary axis of symmetry corresponds really with a molecular arrangement of rhombic symmetry. In any case with a space-lattice, which is relatively close to a regular arrangement: for, as already mentioned, it was impossible till now, to state goniometrically any deviation of the pure regular crystal-form. However, the Röntgenogram shows this deviation with certainty, may it be only by small differences, while a misleading similarity or analogy with true regular symmetry remains present. This fact proves, that in problems of this kind, in many cases the method of the RÖNTGEN-patterns will be of higher value, than the different methods used up to this date.

§ **5**. The described experiments have thus demonstrated the fact, that by heating to 266° C., simultaneously with its optical isotropy, the boracite shows a slight molecular re-arrangement. The question, if the dimorphism of the boracite is connected with a change in its molecular arrangement, must, after what is found here, doubtlessly be answered in the affirmative. ^{1})

It makes only little difference or none in this question, whether the obtained images correspond perhaps only to the exclusive action of one single kind of the atoms, constituting the chemical molecule of boracite. For every kind of atoms of the molecule must be the structure-unit of an individual space-lattice, and all those intergrown space-lattices must be either congruent, or equal with respect to

---

1) Remarkable is also the *granular* character of the central spot on these photographs: experiment taught us, that this fact is connected with the presence of the two aluminium-screens M and N in the way of the RÖNTGEN-rays. Especially remarkable is the more or less regular hexagonal of hexaradiant shape of these spots. Such an hexagonal image was also obtained by means of a thin aluminiumplate alone, about 1,55 m m. thick. It is not improbable, that this fact is connected in some respect with the octahedral crystalform of the aluminium; perhaps the hexagonal image corresponds to six octahedron-faces as directions of preference for the RÖNTGEN-rays.

their symmetry, and at least in conformity with each other, with rational proportions of their linear distances; and they must also remain so, if their aggregation shall be crystallographically a possible one. For that reason the changes in symmetry of one of these space-lattices, must be connected with the same changes in the other ones; it can hardly be hazardous, to conclude from the changes in the Röntgenogram of one of them, with regard to the changes of the other space-lattices. Besides it will seem somewhat improbable with respect to the relatively slight change in molecular arrangement, that at the same time no further change should accompany it, which takes place within the domain of the composing molecules themselves. For the birefringence is, even just a little below the inversion-temperature, again very strong, but disappears at 266° C. quite suddenly. It is difficult to believe, that so great a change could only be attributed to the apparently not very great change in the molecular arrangement. The conception, that the optical properties partly, if not greatly, must be caused by the anisotropy of the composing molecules themselves; more than by the structure of their molecular aggregation, is often defended, just because it is able to give a clear idea of the nature of optically-anomalous crystals. It is true; our experiments have once more proved, that doubtlessly the influence of the molecular arrangement is present; but perhaps it is in this direction of research, that the cases are to be found, which will allow a definitive conclusion with respect to the one or the other of those views.

Experiments with *leucite*, in which the difficulties will be even greater, because of the higher inversion-temperature and the much slower transformation, are at present being made in our laboratories.

Groningen, January 1914.

Mineralogy. — "*On temperature-measurements of anisotropous bodies by means of radiation-pyrometers.*" By Prof. Dr. F. M. JAEGER and Dr. ANT. ŠIMEK. (Communicated by Prof. HAGA).

(Communicated in the meeting of January 31, 1914).

§ 1. In the study of the optical behaviour of white-hot silicates, it accidentally happens that the temperature of the investigated objects is measured by means of the now generally used radiation-pyrometers of WANNER or of HOLBORN—KURLBAUM.

The temperature of the body, as determined in this way, generally cannot coincide with its real temperature; for the mentioned pyro-