UNIVERSITY OF TORONTO STUDIES
GEOLOGICAL SERIES, No. 47

CONTRIBUTIONS TO CANADIAN MINERALOGY, 1942

From the
DEPARTMENT OF MINERALOGY AND PETROGRAPHY
UNIVERSITY OF TORONTO
and the
WALKER MINERALOGICAL CLUB

THE UNIVERSITY OF TORONTO PRESS
TORONTO, CANADA
1942

LONDON:
HUMPHREY MILFORD
OXFORD UNIVERSITY PRESS

PRINTED IN CANADA

TABLE OF CONTENTS

At Professor Parsons' Request the Papers
Contributed to this Issue have been
Arranged for Publication
by Professor Peacock

In Memoriam

THOMAS LEONARD WALKER

M.A., Ph.D., D.Sc., F.R.S.C.

Professor Emeritus of Mineralogy and Petrography
in the University of Toronto

Director Emeritus of the Royal Ontario Museum
of Mineralogy

BORN, DECEMBER 30, 1867
DIED, AUGUST 6, 1942

QUARTZ CONCRETIONS IN GYPSUM AND ANHYDRITE

By G. M. Brownell
University of Manitoba

Quartz concretions occur within gypsum and anhydrite at Amaranth, Manitoba. The occurrence of concretions within evaporites is not generally recognized and Tarr and Twenhofel in Twenhofel (1932, p. 703) refer to the absence of concretionary bodies in rocks of this type as follows: "Concretions occur in all or nearly all varieties of sedimentary rock, evaporation products being the only possible exception and there seems to be no good reason why they should not be there."

However, there are several references in the literature to evaporation products which enclose minerals that possess concretionary characteristics more or less well defined. Even Tarr (1929) recorded the occurrence of concretionary groupings of quartz crystals in gypsum near Acme, N.M., which he described as having been formed as the result of solutions entering the gypsum from the associated sandstones or possibly shales. His description includes some crystalline groups ". . . in which the crystals are arranged in rude radiating clusters, often with one crystal somewhat larger than the others." Likewise at Artesia, N.M., Tarr and Lonsdale (1929) refer to "radiating aggregates" of quartz crystals in the gypsum. Both of these occurrences constitute concretions of epigenetic origin.

The mineral howlite, a silicoborate of calcium, occurs as small rounded embedded nodules made up of flattened prismatic crystals (Dana, 1892). These nodules occur in gypsum and anhydrite in Hants County, Nova Scotia. According to How (1868, 1871), "The nodules are generally about the size of filberts or pigeons' eggs, but occasionally larger." How also described the occurrence of ulexite in these gypsum deposits, stating: "It is in its characteristic nodules sometimes as large as a hen's egg, generally consisting of silky white fibrous crystals."

Biltz and Marcus (1911) refer to the well-known occurrences of boracite nodules in the lower potash beds of the Stassfurt deposits. Nodules of both boracite and hydroboracite, presumably of concretionary origin, are recovered in treating the salts.[1]

[1]A. L. Parsons. Private communication.

One other example, though perhaps more problematical, is the stellate arrangement of gypsum in gypsum at Walton, Nova Scotia, observed by A. L. Parsons.[1] Nodules of selenite in massive gypsum are also mentioned by How (1871), who considered them pseudomorphs after howlite.

GENERAL CHARACTER OF THE DEPOSIT

The Amaranth gypsum deposit (Brownell, 1931) is located near the village of Amaranth, forty miles north of Portage La Prairie, on the west side of Lake Manitoba. Underground mining has been carried on since 1930, the rock-gypsum being shipped to the Winnipeg plant of the Western Gypsum Products, Ltd., owners of the property.

The deposit forms a bed of gypsum and anhydrite thirty-eight feet thick at the main shaft and lies immediately beneath ninety-two feet of glacial till. Presumably the upper portion of the gypsum has been removed by glacial erosion, in fact glacial striae mark the surface of the gypsum where it was exposed in another shaft in the vicinity. The excavation of the sump at the bottom of the shaft reportedly shows the floor of the bottom level to be underlain by three feet of impure gypsum carrying much green clay and limestone. This was followed by twenty-eight inches of green clay below which the sump entered red shale.

The gypsum deposit is a horizontal bed that is divided into three layers: (*a*) an upper gypsum layer about twenty-five feet in thickness; (*b*) a middle layer of anhydrite which averages about four feet in thickness, though it varies somewhat from this figure and is even absent in places; (*c*) a nine-foot layer of gypsum below the anhydrite that constitutes the bottom layer of the deposit.

Throughout the deposit there is an irregular distribution of a buff-coloured limestone which occurs generally in narrow streaks and bands up to six inches thick, though on two occasions mining operations are reported to have removed lenses of limestone seven or eight feet thick and around twenty-five feet or so in horizontal extent. This limestone is a dense fresh homogeneous rock showing no evidence of attack by ground water and is believed to represent a chemical precipitate deposited syngenetically with the original anhydrite.

[1]A. L. Parsons. Private communication.

A striking feature of the Amaranth deposit is the extent of bottom hydration. All of the gypsum production to date has come from this bottom nine-foot layer.

DISTRIBUTION OF CONCRETIONS

Concretions are not abundant in the deposit and only the occasional one can be seen in place. They have been found in the gypsum and within the contained limestone of the bottom layer; they occur in the anhydrite of the middle layer; and it is reported that the diamond drill used for exploring the upper gypsum entered a concretion near the top of this upper layer. It is evident, therefore, that concretions may occur at any level within the deposit.

CHARACTER OF CONCRETIONS

The concretions vary greatly in size, from minute bodies barely visible to the naked eye, to relatively large rounded masses about eighteen inches in diameter. The smallest ones consist of a simple group of minute quartz crystals radiating from a single centre; where several such groups have grown together, a somewhat larger concretion has developed; and with increasing size, many such radiating groups serve as nuclei for the building up of large concretionary

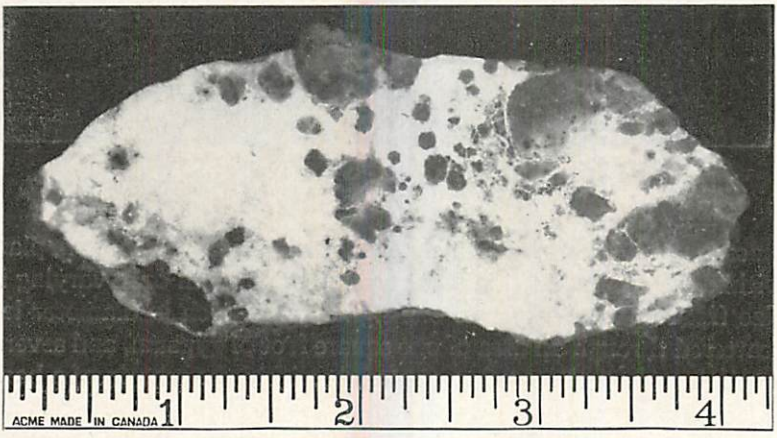

FIG. 1.—Cluster of small quartz concretions in gypsum. Scale of inches.

masses. Some of this latter type look like dense buff coloured chert; others are more vitreous resembling quartzite, and may possess a reddish tint. Because there is no uniformity in their character, several typical varieties are described.

Concretions in Gypsum. (*a*) Among the first concretions encountered were small rounded bodies, red in colour, that look like garnets in the white gypsum (Fig. 1). They have been found in several

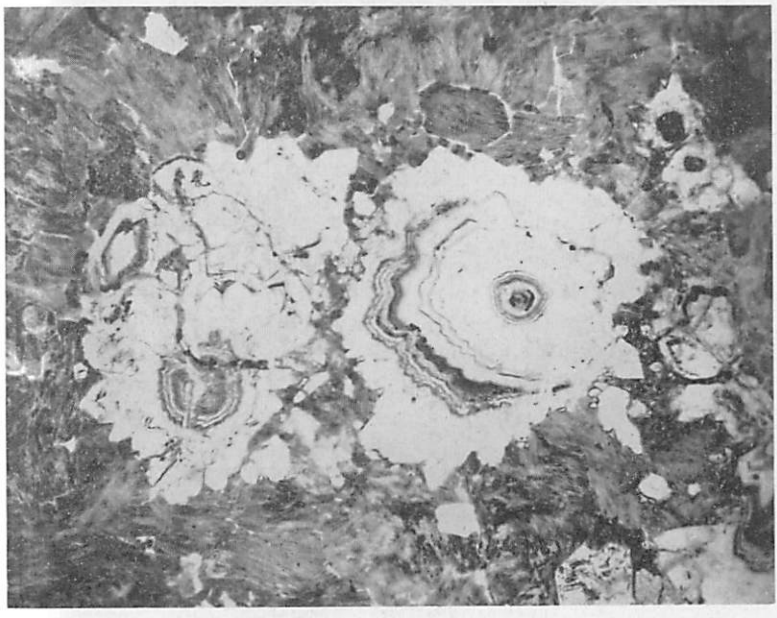

FIG. 2.—Small quartz concretions in gypsum. Plane light. ×29.

masses on the dump but at only one location were they seen in place within the mine. At this point a number of small ones varying in size from minute points to one-eighth of an inch in diameter lay scattered through an area of one square foot of gypsum, and several small ones were observed to occur just within the margin of a band of limestone bordering upon this area. Some of this small red variety are fractured, and when dug out of the gypsum display a surface made rugged by numerous closely spaced terminal pyramids of

quartz. When examined in thin section between crossed nicols, such individual concretions display a radiating structure. Some of them have a central core possessing spherulitic crystallization which is enclosed by successive rings of coarse radiating quartz grains. Figs. 2 and 3 are illustrations of a typical example in which growth rings mark successive stages in the development of the concretion. The central area is pale yellow in colour, which grades into a scalloped

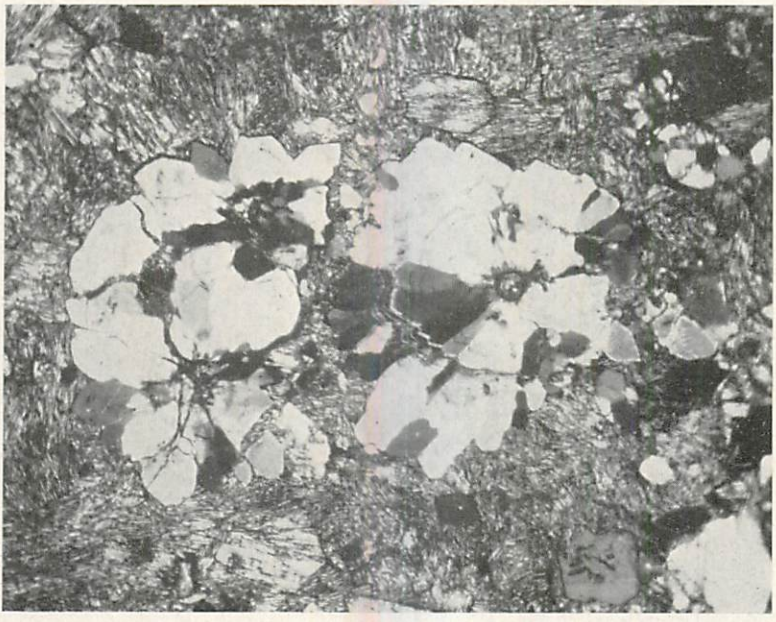

FIG. 3.—Small quartz concretions in gypsum; same area as Fig. 2. Crossed nicols. ×30.

edge of closely spaced concentric yellow lines, followed by others at increasing distances from the centre. The outer rings form a saw-tooth pattern, each point or "saw-tooth" being confined to one quartz grain as if marking the terminus of the crystal at one stage in its development.

Examination with the hand lens of the larger concretions shown in Fig. 1 reveals a more complex structure with several radiating units grouped in one concretion.

(*b*) This specimen from the dump was about six inches across. Its rough surface, when removed from the enclosing gypsum, is made up of small reddish coloured concretions closely spaced. On sawing through the mass, the cross-section shows the internal structure to consist of numerous small reddish concretions similar to those described above, but with the space between them completely filled with white quartz which cements the original group into one large

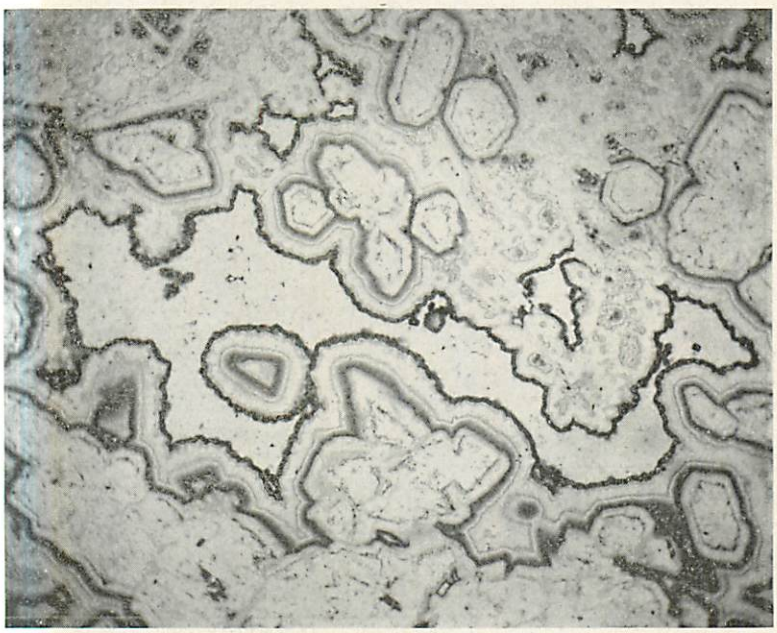

FIG. 4.—Euhedral crystals, bands of chalcedony, and quartz filling, build up large concretions. ×20.

concretion. The cementing quartz is somewhat variable in the coarseness of its texture, but throughout it all are innumerable spherulitic centres, some well developed, others poorly defined, as well as fringes of feather quartz.

(*c*) This specimen formed part of another large concretion from the dump, one partially enclosed by gypsum, vitreous in lustre, and shading from colourless to pink. In thin section this concretion is

found to consist of numerous small euhedral quartz crystals as nuclei around which concentric layers of chalcedony and feather quartz have crystallized to fill the intervening spaces. The crystals range generally between 0.3 and 0.6 mm. in size. Many of these crystals have inclusions of anhydrite as well as a line of fine black inclusions which parallel the outer crystal margin and give it a decided zonal structure. In some of the zoned crystals the outer zone is not in

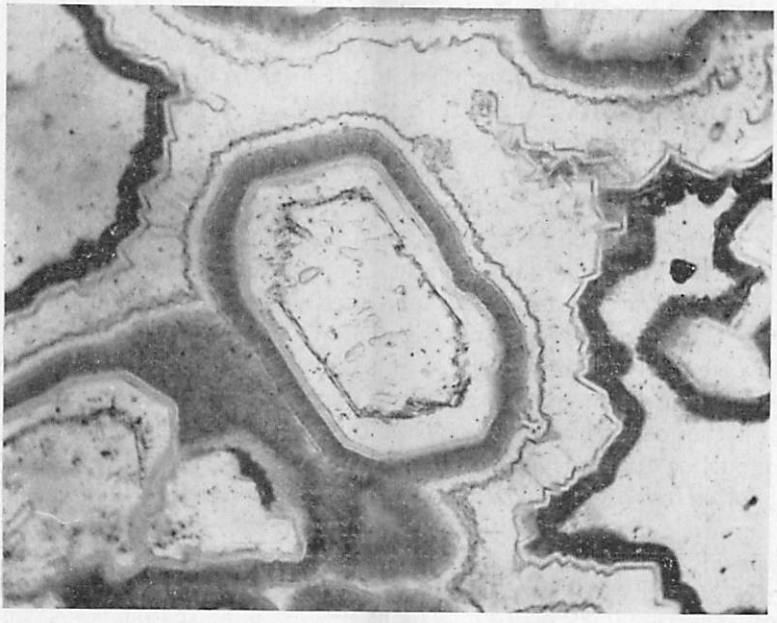

FIG. 5.—Quartz crystals with inclusions of anhydrite, zonal growth, and enclosing fringe of chalcedony (see lower right corner of Fig. 4). ×74.

perfect optical continuity with the inner zone (Figs. 4, 5). Immediately surrounding the crystals is a prominent fringe of chalcedony. In plane light the fringe has a yellowish colour; its refractive index is less than that of the adjacent quartz and its structure is distinctly fibrous.

Besides the euhedral quartz crystals serving as nuclei, there are small clusters of radial or spherulitic quartz that likewise serve as nuclei and are bordered by a fringe of chalcedony.

Concretions in Anhydrite. (*a*) One large angular concretion twelve by eighteen inches was observed in place. It was almost completely within a lens of massive blue anhydrite, only its upper margin being in contact with the overlying gypsum. A large fragment of this concretion was removed and was found to be somewhat sugary in texture. It was porous with numerous small crystal-lined cavities. Some of these cavities have subsequently been filled with selenite. In thin section this mass also reveals numerous small nuclei of quartz with radial structure and concentric lines and fringes of growth. These nuclei are mostly between 0.2 and 0.5 mm. in diameter and clustered together, but the spaces between these clusters are filled with a much coarser crystalline quartz.

(*b*) The massive anhydrite enclosing this large concretion also contains numerous very small concretions, pale yellow in colour. Their maximum size was about 1 mm. in diameter and a concentric structure could be observed with a hand lens in those that were broken. Forty-one of these minute concretions were counted over an area six by eight inches from a specimen of the anhydrite taken near the large concretion described above. A thin section of one of these small concretions shows it to consist of several nuclei with radial growth merging together to form a compound central core, and this central area is enclosed by successive fringes of coarser colourless quartz (Fig. 6).

Concretions in Limestone. The largest concretion found was a rounded mass reportedly about eighteen inches in diameter. This was only one of a number of similar concretions located in the middle of a limestone lens nearly eight feet thick that was contained within the gypsum. Mining operations had just completed the removal of this lens when the writer visited the mine and only fragments of the concretions were available. The rock is a uniformly dense chert-like mass having a light buff colour. From a large fragment two thin sections were prepared.

On examining the thin sections in plane light the faint outlines of rounded or irregular nuclear bodies are discernible; these measure between 0.1 and 0.2 mm. in diameter and constitute nearly one-half of the total area. Between crossed nicols these nuclei are found to consist of a fine granular quartz with a poorly defined radial structure. Also, many of them display one or two narrow growth lines

parallel and close to their outer margin. In addition to these nuclei there are occasional euhedral quartz crystals scattered throughout the mass, all showing prominent strain shadows.

The spaces between these two types of nuclei have subsequently been filled with quartz. Where the spaces were small, a fine granular quartz has been deposited, but where broader spaces existed, the quartz was first deposited as one or more fringes or scalloped bands, leaving a central cavity which was finally filled in by a few

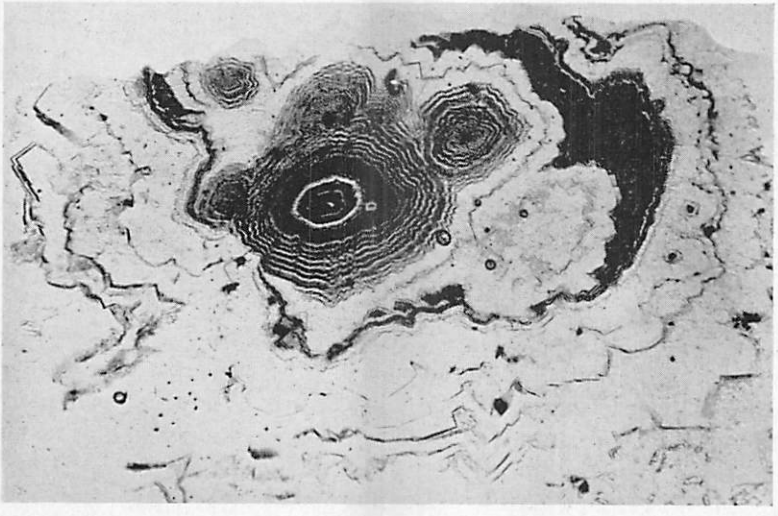

FIG. 6.—Small quartz concretion in anhydrite. Plane light. ×38.

relatively coarse grains. Scattered throughout the section are small patches of fine granular carbonate that appear to be remnants of the limestone that in part encloses the concretion.

ORIGIN OF CONCRETIONS

The occurrence of quartz concretions in gypsum is evidently a rare phenomenon and one would have reason to look for some specific cause in searching for an explanation. The most unusual feature of the Amaranth deposit is the "bottom hydration" of the original bed of anhydrite. Bottom hydration is known elsewhere,

as in the Blaine formation, Oklahoma (Muir, 1934), and several other places, and while no concretions are reported from these deposits, their occurrence in the Amaranth deposit was at first thought to be associated with this condition. It was assumed that the influx of ground water from outside sources would carry an appreciable load of solute and the fixing of the solvent by combining with anhydrite would cause its precipitation. Under such conditions it is remarkable that concretions of some sort are not a common feature of gypsum beds, especially where much greater thicknesses have formed in this manner.

However, no such simple explanation as the above will account for the concretions here described. The penetration of a concretion by the diamond drill in the upper layer of the deposit is proof that they are not a product of bottom hydration; also the discovery of concretions in massive anhydrite as well as a number of them within the massive limestone lenses make it quite evident that their formation is not at all associated with the process of hydration.

The concretions of Amaranth must be considered as syngenetic, that is, they are formed at the same time as the enclosing rock. We may assume with confidence that those now occurring in gypsum were formed within the antecedent anhydrite and suffered no change, other than fracturing in some cases, when hydration took place. Likewise the concretions within the limestone bands were formed at the same time as this structureless carbonate was precipitated. Because of their syngenetic nature, the silica of the concretions must have come from the same source as the enclosing anhydrite and limestone, all of them being chemical precipitates by evaporation of one body of water.

Silica is a minor constituent of gypsum, being present in variable though small quantities. It has been observed as minute grains up to 20 microns in concentrations less than 0.1 per cent, though in the form of opal in concentrations up to 0.5 per cent.[2] Rogers (1910) has recorded the presence of quartz in small (2 or 3 mm.) pale reddish crystals embedded in the massive anhydrite from the salt mines of central Kansas. The quartz concretions at Amaranth do not represent any new constituent within a bed of gypsum, but merely a

[2]United States Gypsum Company, Chicago. Private communication.

common constituent, which here is in greater abundance and coarser form. One needs postulate merely a slightly higher than normal concentration of silica in the water of the original evaporation basin to account for this condition.

Upon the precipitation of silica as evaporation proceeded, concretionary growth was initiated in two ways: either there was the formation of minute spherulites or slightly coarser radial groupings; or the primary development was in the form of small euhedral quartz crystals whose inclusions of anhydrite have already been noted (Fig. 5). With progressive evaporation, successive layers of chalcedony and quartz gradually filled in the spaces between adjacent crystals or radial groups to bind them together into one concretionary mass. However, the relative amount of silica in the deposit is still exceedingly small, a fact that presumably accounts for the sporadic distribution of the concretions.

ACKNOWLEDGMENTS

The writer is indebted to Messrs. H. D. McLaughlin and H. F. R. Baker of the Western Gypsum Products, Limited, and to Mr. M. Tiedman, the mine foreman, for their interest and co-operation which made this study possible; also to Professor A. L. Parsons for reading the manuscript and making suggestions.

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A PRELIMINARY STUDY OF THE ALLOYS OF PALLADIUM AND BISMUTH

By S. V. Burr
Aluminum Company of Canada, Arvida, Quebec
and
M. A. Peacock
University of Toronto

Palladium, a relatively abundant metal of the platinum group, occurs in nature as native palladium (Pd), palladic platinum (Pt, Pd), palladic gold (Au, Pd), potarite (PdHg), stibiopalladinite (Pd_3Sb), and braggite (Pt, Pd, Ni)S. As yet there is no published record of a bismuthide of palladium, either as a mineral or as a laboratory product; a preliminary study of the alloys of palladium and bismuth was therefore undertaken to provide some information on the system Pd-Bi and thus to obtain data which may eventually be of mineralogical interest. The work is limited to a description of the products obtained by fusing the metals in various proportions in a vacuum, with no attempt to determine the phase relations above the ordinary temperature.

Preparation and Examination of the Products

The materials used for this work were coarsely crystallized metallic bismuth (Eimer & Amend, CP) and sheet palladium (Johnson Matthey & Co.) stated to be over 99 per cent Pd and giving the cube-edge $a_0 = 3.882$ Å, in agreement with the precise value 3.8824 ± 0.0003 Å for spectroscopically pure Pd at 18°C. (Owen & Yates, 1933).

Charges of about 1 gm. were prepared by weighing out powdered bismuth and filings of palladium in various atomic proportions,[1] including some simple rational proportions corresponding to possible compounds. The mixed powders were put into silica glass tubes (about 10 mm. inside diameter, 1 mm. wall) previously closed at one end and then drawn down to a passage of 1-2 mm. about 10 cm. from the closed end containing the charge. The tubes were evacuated with a "Megavac" and sealed at the narrow passage.

[1]All proportions given in this paper are atomic proportions.

The tubes were suspended over an open gas flame and observed through a heavy glass shield (1/4-inch "Castwire"). In each case the bismuth melted quickly and suddenly took up the palladium with more or less vigorous evolution of heat, giving a fluid melt which was kept liquid and shaken several times for 10-15 minutes. On withdrawing the flame most of the charges solidified with marked and rapid crystallization. Most of the products were then held for various periods at temperatures somewhat below the melting point, and then allowed to cool in air. Other heat treatments were occasionally given, as mentioned later.

The pellets obtained were broken roughly in halves, usually revealing coarse crystallization and broad cleavage surfaces. One half was mounted on bakelite, ground and polished in the ordinary way, and examined under the reflecting microscope with one nicol and with crossed nicols. Etching was not employed as the constituents and textures stood out clearly on the unetched or naturally tarnished surfaces. Talmage hardness was estimated by applying a needle to the polished sections. Specific gravities were measured on single crystal fragments (10-20 mg.) with the Berman balance. *X*-ray powder photographs of all the products were made with Cu-radiation (Ni-filter). Some single-crystal photographs were also made using cleavage fragments picked from the debris produced by breaking the pellets.

DESCRIPTION OF THE PHASES

In the twenty-six products obtained in the above manner six phases were recognized: the Bi-phase, the compounds α-$PdBi_2$, β-$PdBi_2$, PdBi, Pd_5Bi_3, and the Pd-phase. With exception of the Pd-phase, which shows a considerable range of composition, these phases have very limited ranges, as shown by the fact that the powder patterns show no considerable distortion at intermediate (two-phase) compositions.

With the exception of the Bi-phase which has a reddish tinge, quickly masked by tarnish, the Pd-Bi phases are all white in various degrees with brilliant metallic lustre, especially on cleavage surfaces.

Bi-phase

Bismuth crystallizes in broad anisotropic plates sometimes showing twinning. Polished surfaces quickly develop an iridescent tar-

nish which clearly distinguishes the Bi-phase in the products ranging from Bi to $PdBi_2$. The product Pd_3-Bi_{97} (Fig. 1) already shows crystals of α-$PdBi_2$ and therefore the proportion of Pd tolerated by the Bi-phase is less than 3 per cent. The fact that the Bi-pattern from the product Pd_{20}-Bi_{80} (Fig. 15) is very slightly contracted (lattice expanded, contrary to expectation) as compared with the pattern of Bi (Fig. 13) shows that the Bi-phase can retain a small proportion of Pd in solid solution.

α-$PdBi_2$

The compound $PdBi_2$ was found in two modifications, low temperature α-$PdBi_2$ and high temperature β-$PdBi_2$. α-$PdBi_2$ separated from all the charges between Pd_0 and $Pd_{33.3}$; β-$PdBi_2$ separated from the charges between $Pd_{33.3}$ and Pd_{50}. Charges with the composition $PdBi_2$, cooled in air, showed zoned crystals with cores of β-$PdBi_2$ and margins of α-$PdBi_2$ (Fig. 6), indicating an arrested $\beta \rightarrow \alpha$ inversion.

Homogeneous α-$PdBi_2$ was obtained by annealing a fusion product of that composition below the melting point for 13 days in a furnace and cooling in the furnace. After this treatment the pellet was found to have changed shape, presumably due to the $\beta \rightarrow \alpha$ inversion.

The compound is brittle, the fractured surface showing coarse crystallization and stepped surfaces due to a perfect brilliant cleavage in one direction and a poor cleavage in a second direction. Cleavage fragments thus tend to the shape of thick laths elongated parallel to the intersection of the cleavages and all slightly warped, in keeping with the change of external shape noted above. The polished section (Fig. 4) shows only broad plates and laths of whiteness A (between silver and galena); these are moderately anisotropic (grey to greyish brown). Hardness B (Talmage). Specific gravity 11.53, 11.50 (S.V.B.).

Satisfactory single crystal x-ray photographs have as yet been obtained only from the compound α-$PdBi_2$. A small nearly undeformed cleavage fragment was rotated about the cleavage edge, giving a rotation photograph and Weissenberg resolutions of the zero and first layer-lines. The rotation axis proved to be the sym-

metry axis of a monoclinic lattice in which the smallest permissible cell has the dimensions:

$$a_0 = 12.72,\ b_0 = 4.28,\ c_0 = 5.66\ \text{Å};\ \beta = 102°52'$$

This cell is base-centred as shown by the observed condition: (hkl) present only with $(h + k)$ even. There are no further systematic omissions and therefore the aspect is C^* and the space-group is $C_{2h}^3 - C2/m$, or $C_2^3 - C2$, or $C_s^3 - Cm$, according to the crystal class. With 4[$PdBi_2$] in the unit cell the calculated density is 11.52 as compared with the measured values 11.53, 11.50.

The lattice of α-$PdBi_2$ might also be defined by a larger cell which is rectangular within the limits of good measurements. This cell has the dimensions:

$$a_0' = [201] = 24.80,\ b_0' = [010] = 4.28,\ c_0' = [001] = 5.66\ \text{Å}$$

and a volume which is double that of the base-centred cell. The lamellar twinning noted in the polished section is presumably due to reflection in the axial planes $b'c'$ or $a'b'$ of the rectangular cell. With reference to the base-centred cell these planes of pseudo-symmetry and probable twinning are (100) and ($\bar{1}02$). The perfect cleavage is (100); the poor cleavage is apparently ($\bar{1}02$), giving a feeble reflection on the goniometer at 89°50′ from (100), calculated 90°00′.

TABLE 1

α-$PdBi_2$: *X*-RAY POWDER DATA; Cu/Ni

I	*d*	*I*	*d*	*I*	*d*	*I*	*d*
3	6.26 Å	3	1.687 Å	1	1.238 Å	½	0.948 Å
3	3.16	4	1.635	½	1.221	½	0.940
1	3.11	1	1.614	½	1.196	1	0.930
6	2.98	2	1.584	4	1.175	½	0.910
5	2.81	7	1.549	½	1.151	1	0.904
10	2.76	2	1.491	3	1.113	1	0.896
5	2.48	2	1.447	3	1.070	½	0.886
3	2.34	4	1.415	½	1.046	½	0.849
8	2.20	½	1.334	1	1.028	1	0.842
4	2.14	½	1.289	½	1.012	3	0.831
4	2.08	1	1.276	3	0.976	½	0.825
1	1.879	1	1.251	½	0.960	1	0.818
						½	0.812

Table 1 gives the spacings and relative visual intensities of the *x*-ray powder pattern of α-$PdBi_2$ (Fig. 17). As further work on the

structure of this compound is contemplated the full indexing of this pattern need not be given here; the following correspondence between measured and calculated spacings will give sufficient verification of the powder pattern and the cell dimensions:

TABLE 2

α-$PdBi_2$: SOME MEASURED AND CALCULATED SPACINGS

hkl	*d* (calc.)	*d* (meas.)	*hkl*	*d* (calc.)	*d* (meas.)
(200)	6.20 Å	6.26 Å	(12.0.0)	1.033 Å	(1.028) Å
(400)	3.10	3.11	(14.0.0)	0.886	0.886
(600)	2.07	2.08	(020)	2.14	2.14
(800)	1.550	1.549	(040)	1.070	1.070
(10.0.0)	1.240	1.238	(002)	2.76	2.76

β-$PdBi_2$

Homogeneous β-$PdBi_2$ could not be obtained from charges with the theoretical composition, even by quenching in water, indicating that the $\beta \rightarrow \alpha$ inversion cannot be completely restrained by this treatment. On the other hand, a charge with the composition $Pd_{34}Bi_{66}$, thus containing a slight excess of Pd, combined with a moderate exothermal reaction and gave very nearly homogeneous β-$PdBi_2$ on cooling in air. This gives a clue to the phase boundaries at the composition $PdBi_2$, but the closer study of these boundaries is beyond the scope of our work.

The fractured surface of β-$PdBi_2$ reveals a perfect mirror-like cleavage (recalling that of joseite, $Bi_4(Te, S)_3$), yielding flexible folia on probing with the needle. The polished section (Fig. 5) shows broad plates of β-$PdBi_2$ separated by narrow seams of lighter α-$PdBi_2$ with a few central threads of a tarnished phase (Bi). β-$PdBi_2$ has whiteness A (but slightly darker than α-$PdBi_2$), moderate anisotropism (light grey to dark grey), hardness B, specific gravity 11.67, 11.66 (S.V.B.).

The *x*-ray powder photograph of β-$PdBi_2$ (Figs. 18, 19) is relatively simple, suggesting an hexagonal or tetragonal structure, but an attempt to index the pattern did not succeed. The observed spacings and intensities are given in Table 3.

The non-cubic α-$PdBi_2$ and β-$PdBi_2$ thus contrast sharply with the antimony analogue $PdSb_2$ which has the pyrite type of structure

TABLE 3

β-$PdBi_2$: *X*-RAY POWDER DATA; Cu/Ni

I	*d*	*I*	*d*	*I*	*d*	*I*	*d*
2	6.49 Å	2	1.676 Å	1	1.181 Å	½	0.982 Å
7	3.25	5	1.616	2	1.162	1	0.954
10	2.64	1	1.593	4	1.109	3	0.925
8	2.37	2	1.486	½	1.083	1	0.908
2	2.16	4	1.415	½	1.060	1	0.888
4	2.05	3	1.334	½	1.023	2	0.861
3	1.912	2	1.295	½	1.006	2	0.836
						3	0.811

(Thomassen, 1928) also found in RuS_2, OsS_2, and $PtAs_2$ (Ewald and Hermann, 1931). PdS_2, on the other hand, gives a pattern rich in lines, doubtless excluding the pyrite type (Biltz and Laar, 1936).

PdBi

This compound separated from charges with compositions between Pd_{34} and Pd_{62}. A charge with the composition Pd_{50}-Bi_{50} combined violently on heating, giving a red flash. The product was annealed 3/4 hour and cooled in air.

The compound is brittle, giving a stepped fracture surface due to three non-equivalent cleavages in one zone. One of these is broad, relatively easy, but uneven; the second is good and at right-angles to the first (89°59′); the third is fair and is inclined to the broad cleavage at 36°16′. The polished section (Fig. 8) shows a coarse mosaic of homogeneous grains with whiteness A, moderately strong anisotropism (bluish grey to brown grey), and hardness B. Specific gravity 12.85 (S.V.B.).

The spacings and intensities of the powder pattern of PdBi (Fig. 21) are given in Table 4.

The cleavages of PdBi and some unsatisfactory single crystal photographs admit orthorhombic or monoclinic symmetry. The provisional cell dimensions do not show orthohexagonal relations and therefore PdBi is apparently not isostructural with PdSb, which has the niccolite type of structure (Thomassen, 1928), or with PdS, (Pt, Pd, Ni)S (braggite), or PtS (cooperite), which have tetragonal structures (Bannister, 1932).

TABLE 4

PdBi: *X*-RAY POWDER DATA; Cu/Ni

I	*d*	*I*	*d*	*I*	*d*	*I*	*d*
3	3.36 Å	6	1.679 Å	1	1.221 Å	½	0.952 Å
10	2.65	4	1.638	½	1.210	2	0.932
2	2.50	½	1.583	5	1.174	2	0.895
½	2.37	1	1.478	½	1.131	2	0.867
4	2.25	5	1.395	1	1.084	7	0.856
8	2.16	3	1.329	2	1.034	½	0.849
½	1.786	5	1.269	½	1.004	½	0.840
				1	0.977	1	0.826

Pd_5Bi_3

This compound was found in charges with compositions Pd_{60} to Pd_{67} and was obtained as a homogeneous product from a fusion of $Pd_{62.5}$-$Bi_{37.5}$ annealed near the fusion temperature for 24 hours.

Pd_5Bi_3 is brittle and somewhat tougher than the previously described products, the broken surface showing one good but difficult cleavage and a fracture of conchoidal character. The polished section (Fig. 10) is homogeneous with whiteness A and weak anisotropism revealing no grain structure. In other preparations the Pd_5Bi_3 component has fairly strong anisotropism, suggesting that the homogeneous product was cut along a nearly isotropic section in a single crystal. The hardness is C, the specific gravity 12.52, 12.50 (S.V.B.).

The spacings and intensities given by the *x*-ray pattern (Fig. 22) are listed in Table 5.

TABLE 5

Pd_5Bi_3: *X*-RAY POWDER DATA; Cu/Ni

I	*d*	*I*	*d*	*I*	*d*	*I*	*d*
3	3.23 Å	1	2.17 Å	2	1.519 Å	2	1.228 Å
2	2.92	1	2.02	3	1.453	3	1.200
1	2.64	1	1.840	1	1.417	½	1.157
2	2.51	½	1.760	1	1.384	2	1.116
5	2.34	2	1.622	2	1.317	1	0.928
4	2.31	1	1.591	2	1.287	1	0.909
10	2.24	1	1.533	1	1.261	1	0.879
						2	0.857

We know nothing of the symmetry of Pd_5Bi_3 beyond the fact that it is not cubic (cleavage, anisotropism). In the system Pd-Sb Sander (1912) found α-Pd_5Sb_3 inverting to β-Pd_5Sb_3 at 530°, but Grigorjew (1932) obtained inhomogeneous annealed products at this composition.

Pd-phase

The range of composition of the Pd-phase is indicated by the product of a charge Pd_{75}-Bi_{25} which was fused and annealed for 3/4 hour. The product is tough and somewhat malleable, breaking with difficulty, like a fine-grained metal.

The polished section (Fig. 12) shows an aggregate of elongated grains with whiteness A, separated by a small amount of interstitial dark grey material. The main mass is homogeneous and weakly anisotropic. The hardness is C.

The powder photograph (Fig. 23) shows a diffuse and strongly contracted Pd-pattern (Fig. 24) with one distinct extra line apparently corresponding to the strongest line of the pattern of Pd_5Bi_3 (Fig. 22). The cube-edge given by the contracted pattern is $a_0 = 4.070 \pm 0.005$ Å as compared with $a_0 = 3.882$ Å for pure Pd.

The product Pd_{75}-Bi_{25} is thus essentially a solid solution of Bi in Pd with a face-centred cubic structure in which one Pd-atom in four, or one atom per unit cell, is replaced by Bi. The presence of a small amount of a second phase indicates that 25 per cent Bi is slightly in excess of the limiting Bi-content of the Pd-phase. The weak anisotropism may be related to distortion of the cubic lattice at the limiting Bi-content; the same effect has been noted in natural antimonial silver (Sb 6.78 per cent) representing the Ag-phase at the limiting Sb-content (Peacock, 1940).

These observations on Pd_{75}-Bi_{25} again contrast with the analogous phase in the Pd-Sb system. Here Sander (1912) found a compound Pd_3Sb which showed an $\alpha \rightarrow \beta$ inversion at 950°. In the solid state Pd dissolved up to 15 wt. per cent (13.4 at. per cent) Sb. Stibiopalladinite Pd_3Sb is isotropic (Wagner, 1929), but Schneiderhöhn, in Wagner (1929), obtained a columnar structure in etched polished sections. A comparison with the artificial product has apparently not been made.

It remains to mention the possible existence of one more Pd-Bi compound, between $Pd_{62.5}$ (Fig. 10) and Pd_{75} (Fig. 12), represented

by the prismatic crystals in the two-phase product $Pd_{66.7}$ (Fig. 11). From the powder photographs this product can be interpreted as crystals of Pd,Bi in a ground of Pd_5Bi_3 and it is possible that the tendency to elongation shown by the grains of Pd,Bi in Fig. 12 might result in a prismatic habit in free crystals. On the other hand such elongation seems improbable in an essentially cubic crystal, and since the powder patterns in this region are neither strong nor rich in lines, we cannot exclude the existence of a further compound in the range in question.

NOTES ON THE FUSION PRODUCTS AND EXPLANATION OF THE FIGURES

In conclusion it will be useful to give condensed descriptions of the fusion products, with some details of the intergrowths obtained at various intermediate (two-phase) compositions. The bulk compositions of the products are given in atomic percentages, and unless otherwise stated the products were obtained by fusion followed by annealing for 3/4—1½ hours somewhat below the crystallization temperature.

These notes will also serve to explain the illustrations which represent a selection of the polished sections and powder photographs. Figures 1-12 are micrographs of the unetched or naturally tarnished polished sections in vertical reflected light. Each figure represents a square of 1.00 mm. on the polished section. Figures 13-24 are x-ray powder photographs (full-size reproductions of contact prints) taken with Cu-radiation (Ni-filter) in a camera of radius $360/4\pi$ mm. (1 mm. on the film = $1°\theta$).

Pd_0-Bi_{100}—No observations were made on pure Bi; the powder photograph (Fig. 13) represents native bismuth from Cobalt, Ontario.

Pd_3-Bi_{97}—Sparse radiating needles and laths of α-$PdBi_2$ in large plates of tarnished Bi (Fig. 1). The powder photograph shows the pattern of Bi with two faint lines corresponding to the strongest lines of α-$PdBi_2$.

Pd_{10}-Bi_{90}—Stout laths and small crystals of α-$PdBi_2$ in broad plates of tarnished Bi. The powder pattern (Fig. 14) shows the pattern of Bi and several distinct lines of α-$PdBi_2$.

$Pd_{16.7}Bi_{83.3}$—Larger crystals (note the euhedral monoclinic (010)-section) of α-$PdBi_2$ in a matrix of tarnished Bi with microlites of α-$PdBi_2$ (Fig. 2). The powder photograph shows the patterns of Bi and α-$PdBi_2$ in about equal strength.

Pd_{20}-Bi_{80}—Close network of laths of α-$PdBi_2$ in a ground of tarnished Bi and needles of α-$PdBi_2$. The powder photograph (Fig. 15) shows a slightly contracted Bi-pattern and an equally strong pattern of $PdBi_2$.

Pd_{25}-Bi_{75}—Abundant crystals of α-$PdBi_2$ in a eutectic of Bi and α-$PdBi_2$ (Fig. 3). The powder photograph (Fig. 16) shows a strong pattern of α-$PdBi_2$ and a weak pattern of Bi.

Pd_{28}-Bi_{72} and Pd_{31}-Bi_{69}—Show further increase in the proportions of α-$PdBi_2$ and decrease of the Bi-matrix with corresponding weakening in the Bi-pattern.

$Pd_{33.3}$-$Bi_{66.7}$ (annealed for 13 days)—Homogeneous α-$PdBi_2$ (Fig. 4, crossed nicols); pattern of α-$PdBi_2$ (Fig. 17).

$Pd_{33.3}$-$Bi_{66.7}$ (annealed 1½ hours)—Large crystals with darker cores of β-$PdBi_2$ and lighter margins of α-$PdBi_2$ and scanty tarnished matrix (Fig. 6). A powder photograph from a single crystal, accidentally sampling the homogeneous core, gave the pattern of β-$PdBi_2$ (Fig. 18); a representative sample of the section showed the patterns of α-$PdBi_2$ and β-$PdBi_2$.

$Pd_{33.3}$-$Bi_{66.7}$ (quenched in cold water)—The product is finer grained than the foregoing but similarly constituted.

Pd_{34}-Bi_{66} (annealed for 15 minutes)—Broad plates of β-$PdBi_2$ with narrow seams of α-$PdBi_2$ (Fig. 5, crossed nicols); pattern of β-$PdBi_2$ (Fig. 19).

Pd_{37}-Bi_{63}—Rounded embayed crystals and aligned blebs of PdBi in broad plates of β-$PdBi_2$; pattern of β-$PdBi_2$ with one line of PdBi.

Pd_{40}-Bi_{60} (annealed 6½ hours)—Abundant graphic PdBi in plates of β-$PdBi_2$ (Fig. 7, crossed nicols); the pattern (Fig. 20) shows both constituents.

Pd_{50}-Bi_{50}—Plates of PdBi (Fig. 8, crossed nicols); pattern of PdBi (Fig. 21).

Pd_{60}-Bi_{40}—Globular areas of Pd_5Bi_3 with an irregular network of PdBi (Fig. 9); the pattern shows Pd_5Bi_3 with a few lines of PdBi.

$Pd_{62.5}$-$Bi_{37.5}$ (annealed for 24 hours)—Homogeneous Pd_5Bi_3 (Fig. 10, crossed nicols); pattern of Pd_5Bi_3 (Fig. 22).

$Pd_{66.7}$-$Bi_{33.3}$—Prismatic crystals of the Pd-phase, or a new compound, in a ground of Pd_5Bi_3 (Fig. 11); the pattern can be interpreted as Pd_5Bi_3 with lines of the Pd-phase.

Pd_{75}-Bi_{25}—Granular aggregate of the Pd-phase (Pd,Bi solid solution) with scanty matrix (Fig. 12); the pattern (Fig. 23) is a contracted Pd-pattern with an extra line.

Pd_{100}-Bi_0—Powder pattern of Pd (Fig. 24).

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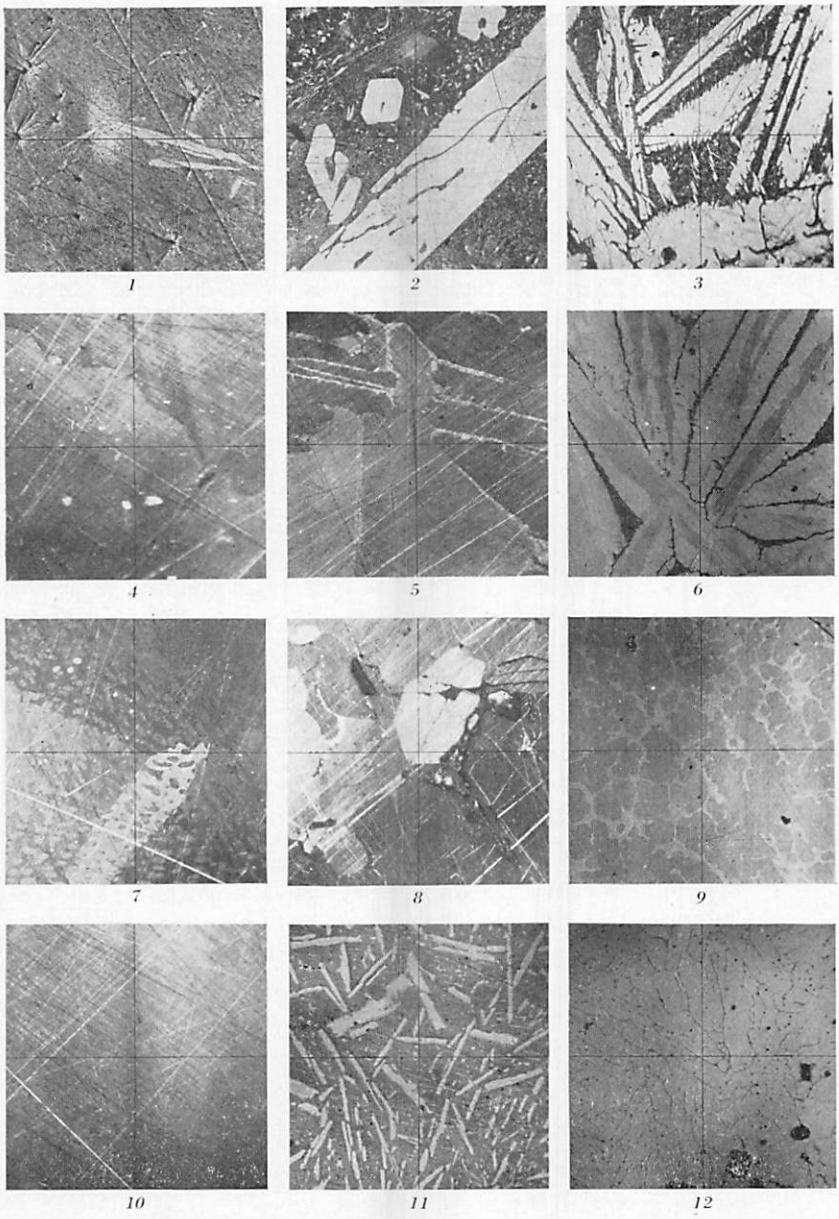

FIGS. 1-12.—Alloys of palladium and bismuth: polished sections. (See "Notes on the fusion products and explanation of the figures.")

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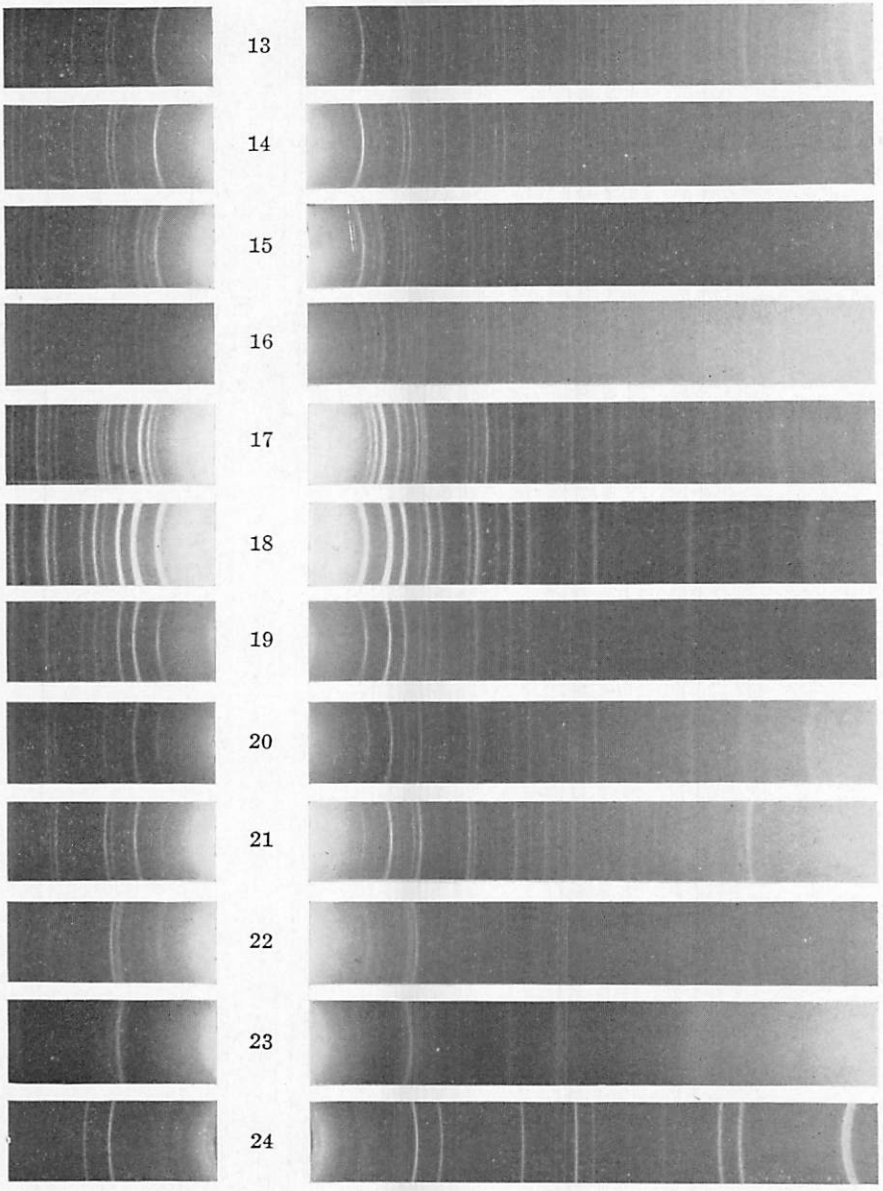

FIGS. 13-24.—Alloys of palladium and bismuth: *x*-ray powder photographs. (See "Notes on the fusion products and explanation of the figures.")

DERIVATION OF THE THIRTY-TWO POINT-GROUPS

By J. D. H. Donnay
Université Laval, Quebec

INTRODUCTION

In view of the adoption of the international symmetry symbols (Mauguin, 1931), it is desirable to have a method of deriving the 32 point-groups (crystal classes) that will lead to the new symbols. No simple derivation of this kind is available that I know of. The purpose of this paper is to present one.

The new symbolism defines the axis of composite symmetry (or alternating axis) as an *inversion axis*, and the corresponding operation as a *rotatory-inversion* (or rotoversion). Previously the *reflection axis* and the *rotatory-reflection* (or rotoflection) had been used mostly.[1] Inversion axes, first used by Liebisch (1896), were advocated by Hilton (1906), who pointed out their formal advantage, namely that the period of the singular axis is always 3 in crystals whose lattice may be rhombohedral or hexagonal, and 6 in crystals whose lattice can only be hexagonal.

The first step in deriving the 32 point-groups is to establish that there are only two kinds of symmetry operations: the *rotation* and the *rotatory-inversion*.[2] No proof of this fundamental proposition is to be found in the current text-books of mineralogy, and even some advanced books on crystallography omit it, probably because it is considered too difficult. A proof, requiring only elementary mathematics,[3] will be given in this paper.

[1]A. F. Rogers (1926) proposed using both kinds of alternating axes: reflection axes with periods 4 and 6, inversion axis with period 6. The advantage is that the number indicating the *period of the axis* also expresses the *order of the group*. The period n of the axis is defined by its smallest rotation: $360°/n$. The order of the group is the number of symmetry operations in the group, or the number of equivalent faces in general position. For a more complete discussion of this topic, see Donnay (1935).

[2]Or the rotatory reflection, if one chooses that alternate definition of the operation of the 2nd kind.

[3]The proof given by Ewald (1933) demands the following mathematical prerequisites: vector calculus, linear transformations and determinants, solution

The second step is to prove that the period n of a rotation axis must be an integer, and that the only axes of symmetry possible in crystals are the rotation axes 1, 2, 3, 4, 6, and the inversion axes $1, 2, \bar{3}, \bar{4}, \bar{6}$.

The third step is to combine the above symmetry elements in all possible manners. This is the actual derivation. It is greatly facilitated by the fact that the co-existence of certain symmetry elements automatically requires (or excludes) the presence of certain others. The necessary results are presented in the form of eight theorems on symmetry.[4] In the proposed derivation of the 32 point-groups, the axes and groups of axes are combined with the *centre* ($\bar{1}$) and with *mirrors* ($m = \bar{2}$). The $\bar{3}$-axis is not explicitly considered—it appears eventually each time a 3-axis is combined with the centre ($\bar{3} = 3 + \bar{1}$). The $\bar{6}$-axis is considered for convenience, although it is not an independent element of symmetry ($\bar{6} = 3/m$), because this leads more directly to the adopted classification.

SYMMETRY

Definitions. All parallel lines have the same direction. A direction AB is either *homopolar* or *polar*, according as the two senses in which it may be travelled (AB and BA) are, or are not, equivalent. Certain crystals possess directions different from all others in the crystal; such a direction is called a *singular direction.* A crystal direction may be polar for one property, and homopolar for another.

A crystal in which all directions are singular and polar, with

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of the 3rd degree equation, complex variables and interpretation in the complex plane.

The definition of symmetry proposed in this paper is that of Ewald, modified and, it is hoped, improved by the explicit consideration of the polarity or homopolarity of singular directions.

[4]This procedure was used by Bravais (1849), whose theorems, however, were only concerned with rotation axes, mirrors, and centre of symmetry. A later treatment of the French School (see Friedel, 1926, pp. 33-36) included consideration of the composite symmetry, in the form of Curie's *planes of alternating symmetry* (1884); fourteen theorems were necessary. An interesting attempt at simplification was made by Swartz (1909), who used rotatory-reflection. Some of the proofs of his theorems unfortunately lack rigour, but his paper is stimulating; it contains, moreover, an extensive bibliography and a very scholarly review of the historical development of the subject.

respect to a certain property, is said to be *asymmetrical* (or to lack symmetry) as regards that property. A crystal in which not all directions are singular and polar, with respect to a given property, is said to be *symmetrical* (or to have symmetry) as regards that property. In other words: as regards the property considered, to any non-singular direction in a symmetrical crystal there exists one, or more than one, equivalent direction. A singular direction AB, if polar, has no equivalent direction; if homopolar, is equivalent to its "counter-direction" BA.

By the *symmetry of a crystal*, with no qualification as to which property is considered, is meant the symmetry common to all its properties (the equivalence of directions must hold true for any property). It is a law of observation that all crystals of the same substance (same chemical compound, and, in case of polymorphism, same modification) show the same symmetry. This fact is not evident *a priori*, nor could it have been predicted with any degree of certainty. The *Law of Constancy of Symmetry*[5] is not given due recognition in most text-books, which seem to take it for granted. Yet this law is the reason that makes it worth while to study the symmetry of crystals.

A natural crystal, on account of accidental conditions of growth, is often *malformed*, in that physically similar faces have neither the same size nor the same shape. In order to emphasize equivalent directions, the *sheaf of face normals* (passed through any one point in the crystal) is substituted for the crystal itself in the study of its symmetry.

SYMMETRY OPERATIONS

A symmetrical crystal has been defined by the fact that it possesses equivalent directions or, if all its directions are singular, that they are homopolar. An operation which, applied to a symmetrical crystal, brings every direction into coincidence with an equivalent direction[6] is called a *symmetry operation*. The expression "bringing the crystal to *self-coincidence*" is often used; it is quite justifiable if,

[5]Not to be confused with the "Law of Symmetry," found in many older books. It is known that this so-called law actually is not a law, but a definition (and a poor one, at that) of symmetry.

[6]The sense being taken into account for polar directions.

by crystal, is meant the sheaf of face normals, for a symmetry operation brings every line of the sheaf into coincidence with an equivalent line. Two consequences follow immediately:

(1) In any symmetry operation, *the apex* O *of the sheaf remains fixed*: it is a singular point in the sheaf, hence it must be brought to coincidence with itself.

(2) In any symmetry operation, *the angle between any two lines of the sheaf must remain unchanged.* Thus if the operation carries the lines OA, OB, OC, . . . to OA′, OB′, OC′, . . . , we must have A′OB′ = AOB, A′OC′ = AOC, and so on. For otherwise, not all the pairs of lines OA, OA′; OB, OB′; OC, OC′; . . . would consist of equivalent lines. Letting OB, OB′; OC, OC′; . . . be pairs of equivalent lines, for instance, and assuming A′OB′ $\neq$ AOB, A′OC′ $\neq$ AOC, . . . , then OA′ would bear a different relationship to OB′, OC′, . . . , than OA to OB, OC, . . . , so that OA′ could not be equivalent to OA, and the operation would not be a symmetry operation.

THE TWO KINDS OF SYMMETRY OPERATIONS

The ultimate reason why there are only two kinds of symmetry operations is that a system of three coordinate axes (Cartesian axial cross) can be oriented in two ways only. The system may be either[7] left-handed (Fig. 1) or right-handed (Fig. 2). Before this simple

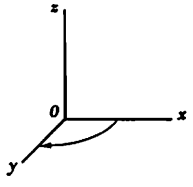

FIG. 1
Left-handed axial cross.

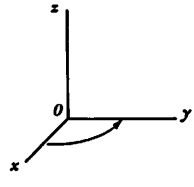

FIG. 2
Right-handed axial cross.

[7]Here is a simple rule to tell the orientation of an axial cross. Notice in which sense the positive half-axis O*x* must be rotated (in the *xy*-plane) about the origin to be brought onto the positive half-axis O*y* by the shorter route. You may close either your left or your right hand in that same sense, while holding your thumb pointed towards the positive end of the *z*-axis. The axial cross is, accordingly, left-handed or right-handed.

concept can be used, however, it is necessary to show that *a symmetry operation is nothing else than a transformation of coordinate axes.*

A symmetry operation, which brings the lines OA, OB, OC, . . . into coincidence with the lines OA′, OB′, OC′, . . . respectively, establishes a one-to-one correspondence between the former and the latter lines. A transformation of coordinate axes is the mathematical way of expressing this relation, for such a transformation relates a line with given direction cosines in the old system of axes to the line that has the same direction cosines referred to the new axes. For convenience, let the initial set of axes be taken as Cartesian (axes mutually perpendicular), with their origin at the apex of the crystal sheaf. Now, if the transformation of coordinate axes is to express a symmetry operation, any transformed line OA′ must be equivalent to the corresponding original line OA; moreover, the new axes are subject to two restrictions.

(1) *The new axes must have the same origin as the old axes.* Indeed we have seen that the apex of the sheaf, being a singular point, must transform into itself. Hence the coordinates $x = 0$, $y = 0$, $z = 0$ must designate one and the same point in both systems of axes.

(2) *The new axes must be mutually perpendicular, like the old axes.* Otherwise the angle A′OB′ between any two transformed lines OA′ and OB′ would not be equal to the angle AOB between the corresponding original lines OA and OB.

The only kinds of axial transformations to be considered are therefore those which make a Cartesian axial cross go into another Cartesian axial cross with the same origin. There are two such kinds of transformations, according as the new axial cross is, or is not, oriented like the old one. They represent the only two possible kinds of symmetry operations.

AXIAL TRANSFORMATION OF THE 1ST KIND

Consider, in stereographic projection (Fig. 3), two Cartesian axial crosses, both right-handed and with the same origin: $Oxyz$ and $Ox'y'z'$. (The point O is the centre of the sphere of projection.) For convenience let Oz' be vertical. It is always possible to pass from one ($Oxyz$) to the other ($Ox'y'z'$) by means of two reflections.

Reflect the axial cross $Oxyz$ (right-handed) in the plane AB that perpendicularly bisects the point-pair zz'. It becomes, say, Ox_1y_1z'

(left-handed). Note that, since Oz has been converted into Oz′, the new axes Ox_1 and Oy_1 lie in the equatorial plane. Now (Fig. 4) the meridional plane CD that bisects the angle y_1Oy' also bisects the angle x_1Ox'. Reflect in CD, and Ox_1y_1z' (left-handed) becomes $Ox'y'z'$ (right-handed) as desired.

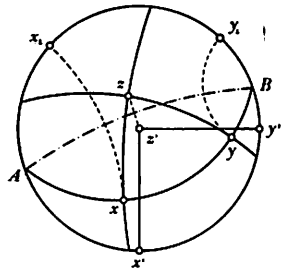

FIG. 3
First reflection.

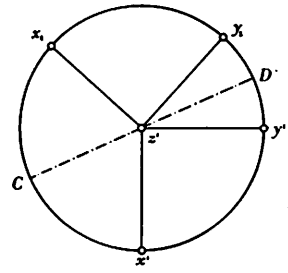

FIG. 4
Second reflection.

It is easy to see that two reflections in intersecting planes are equivalent to a rotation, about the line of intersection, through twice the angle between the planes. The first kind of axial transformation (or of symmetry operation) is thus a *rotation*.[8]

AXIAL TRANSFORMATION OF THE 2ND KIND

Consider now two Cartesian axial crosses with the same origin: one right-handed, Oxyz; the other left-handed, OXYZ. Consider also (Fig. 5) an auxiliary axial cross $Ox'y'z'$, obtained by taking as positive directions for its axes the negative ends of the axes OX, OY, OZ, respectively.

Since OXYZ is left-handed, $Ox'y'z'$ is right-handed. It is always possible to pass from Oxyz (right-handed) to $Ox'y'z'$ (right-handed) by a rotation (as shown above), then to pass from $Ox'y'z'$ (right-handed) to OXYZ (left-handed) by changing the signs of all three axes, that is to say by inverting through the origin. The complete transformation is thus a combination of a rotation about a straight

[8]Converting Oxyz into $Ox'y'z'$ by two reflections is simpler than by three rotations. It also obviates the necessity of introducing Euler's theorem at this stage.

line with an inversion through a point on this straight line. This second kind of axial transformation (or of symmetry operation) is thus a *rotatory-inversion.*

REMARK.—The auxiliary right-handed system $Ox'y'z'$ could also be chosen by changing the sign of only one of the axes OX, OY, OZ; for instance (Fig. 6), by taking the negative end of OZ as positive end of Oz'. This would lead to defining the axial transformation of the second kind as a rotatory-reflection (rotation combined with reflection), instead of a rotatory inversion. The latter definition is preferred.

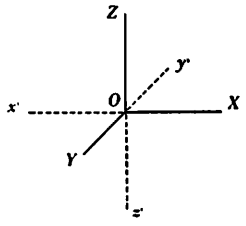

FIG. 5

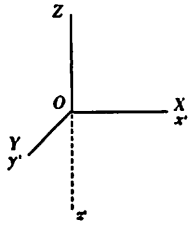

FIG. 6

Relation between a left-handed (OXYZ) and a right-handed ($Ox'y'z'$) Cartesian axial crosses: inversion or reflection.

SYMMETRY ELEMENTS

If a symmetry operation is applied 2, 3, . . . n times in succession, the result is a symmetry operation, for the crystal is thereby brought to self-coincidence. This is conveniently expressed:[9] *the powers of a symmetry operation are symmetry operations.* Likewise if 2, 3, . . . n symmetry operations are applied in succession, the result is again self-coincidence. This is what is meant by: *products of symmetry operations are symmetry operations.* If an operation transforms a figure F into F′, the operation required to transform F′ back into F is called its *inverse operation.* The product of an operation by its inverse is called the *identical operation*; it brings any figure back to its original position.

All the powers of a given symmetry operation constitute a *symmetry element.*

There are two kinds of symmetry elements, corresponding to the two kinds of symmetry operations.

[9]Borrowing the terminology from the mathematical theory of groups.

Let $\omega = 360°/n$ be the smallest angle through which a given crystal can be rotated about a straight line to be brought to self-coincidence. All the powers of this rotation (that is to say the rotations through ω, 2ω, . . . , etc.) form a symmetry element called a *rotation axis of symmetry*. (The straight line about which the rotation takes place is also termed rotation axis.)[10]

Consider now a rotatory-inversion. Again, let $\omega = 360°/n$ be the smallest angle through which the crystal is rotated in the course of a rotatory-inversion that brings it to self-coincidence. All the powers of this rotatory-inversion form a symmetry element called an *inversion axis of symmetry*. (The straight line about which the rotation takes place, combined with the point on that line through which the inversion is effected, is also termed inversion axis.)[10]

In symmetry notation, a rotation axis is represented by its period n and an inversion axis, by its period surmounted by a bar $\bar{n}$ (pronounced[11] "minus n," "inversion n," or "n bar"). For short, we may conveniently speak of an "n-axis" for a rotation axis and a "$\bar{n}$-axis" for an inversion axis.[12] An inversion axis with an even period will be represented by $\overline{2n}$.

POSSIBLE AXES OF SYMMETRY

The trend of the reasoning is as follows: Prove first, as a lemma, that the period n of a rotation axis must be an integer. Then, prove the theorem that no rotation axes other than 1, 2, 3, 4, 6 are possible

[10]The difference between the two meanings is perhaps more apparent than real. The rotation axis of symmetry, for instance, is not only a straight line, but a straight line about which rotations can take place. The concept of the symmetry operations cannot be dissociated from that of the line itself. The 2-axis really stands for two rotations (angles 0 and 180°); the 4-axis, for four rotations (angles 0, 90°, 180°, 270°); and so on. This explains why we speak of "an axis *including* another axis" (when the symmetry operations of the latter are included among those of the former). For example, when a line is, at the same time, the direction of a $\bar{4}$-axis and of a 2-axis, we say that "the $\bar{4}$-axis includes the 2-axis." Likewise a 4-axis includes a 2-axis; a 6-axis includes a 2-axis and a 3-axis; a $\bar{3}$-axis includes a 3-axis and so does a $\bar{6}$-axis.

[11]"Minus n" recalls the fact that the inversion gives the minus sign to all positive directions; "inversion n" (suggested by Professor D. Jerome Fisher, University of Chicago) is self-explanatory; "n bar" is perhaps the least recommendable expression.

[12]Suggested by Professor M. A. Peacock, University of Toronto.

in crystals. (Proofs of these two points are readily available.) Then, as a corollary, show that the only inversion axes possible in crystals are $\bar{1}$, $\bar{2}$, $\bar{3}$, $\bar{4}$, $\bar{6}$. This is easily proved by remarking that, *in so far as face directions are concerned*, an inversion axis $\bar{n}$ is equivalent to a rotation axis n. Indeed the rotatory-inversion is a rotation through $360°/n$, coupled with an inversion. The direction which a face assumes after the rotation, is not altered by the inversion. Since the restrictions imposed by Haüy's Law of Rationality (or by the lattice) deal only with the directions of faces, the periods of the permissible inversion axes are the same as those of the rotation axes.

INDEPENDENT SYMMETRY ELEMENTS

By means of stereographic projections (projecting a general face and all its equivalent faces, created by the symmetry element), it is easy to show that a $\bar{1}$-axis is equivalent to a *centre*, that a $\bar{2}$-axis is equivalent to a *mirror* (m) perpendicular to the axis, that a $\bar{3}$-axis is equivalent to the combination of a 3-axis and a centre ($\bar{3} = 3 + \bar{1}$), that a $\bar{4}$-axis is irreducible, that a $\bar{6}$-axis could be replaced by a 3-axis and a mirror perpendicular to it ($6 = 3/m$).

The independent symmetry elements are thus: the rotation axes, the centre, the mirror, and the $\bar{4}$-axis. For convenience, the $\bar{6}$-axis will be considered a distinct element in the method adopted for the derivation of the 32 point-groups.

THEOREMS OF SYMMETRY

Definition. A *singular axis* is an axis parallel to a singular direction.

Theorem I: No mirror can be oblique to a singular axis and the only kind of axis compatible with a singular axis is a 2-axis perpendicular to it.

Theorem II: Of the following three elements of symmetry, an even-fold rotation axis, a mirror perpendicular to it, and the centre at their intersection, no two can exist without the third (Fig. 7).

Corollary: A rotation axis with an odd period cannot combine with both a mirror perpendicular to it and the centre. (Otherwise it would have an even period.)

REMARK.—It is not necessary to consider the combination of a 3-axis with a mirror perpendicular to it, since this combination is represented by the $\bar{6}$-axis.

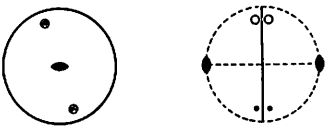

FIG. 7.—Group $2/m$ in two orientations (2-axis vertical or horizontal).

Theorem III: A crystal that possesses an n-axis and one 2-axis perpendicular to it, possesses in all n such 2-axes, intersecting at equal angles ($180°/n$), homopolar and of two different kinds if n is even, polar and of the same kind if n is odd.

This theorem leads (Fig. 8) to the following groups:[13] 2, 222, 422, 32, 622.

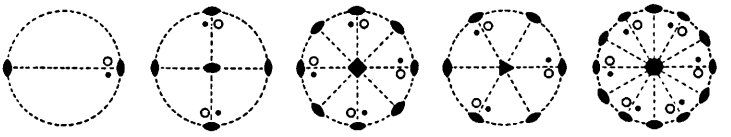

FIG. 8

Group 2 Group 222 Group 422 Group 32 Group 622

Theorem IV: A crystal that possesses an n-axis and one mirror through it, possesses in all n such mirrors, intersecting in the n-axis at equal angles ($180°/n$), homopolar and of two different kinds if n is even, polar and of the same kind if n is odd.

This theorem leads (Fig. 9) to the following groups: m, $2mm$, $4mm$, $3m$, $6mm$.

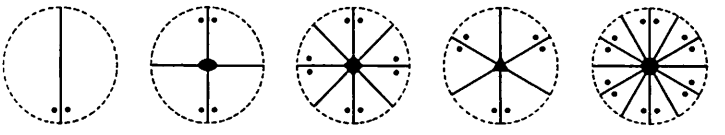

FIG. 9

Group m Group $2mm$ Group $4mm$ Group $3m$ Group $6mm$

Theorem V: A crystal that possesses a $\overline{2n}$-axis and either one 2-axis perpendicular to it, or a mirror through it, possesses in all n

[13]For the explanation of the symbols, see Mauguin (1931), Fisher (1935), or Donnay (1935).

such 2-axes of the same kind and n such mirrors of the same kind. The mirrors bisect the angles between the 2-axes if n is even; they contain the 2-axes if n is odd. The mirrors and the 2-axes are homopolar or polar, according as n is even or odd.

Theorem VI: If a crystal possesses an n-axis, n 2-axes perpendicular to it, and one mirror through it, bisecting the angle between the 2-axes if n is even, containing a 2-axis if n is odd, then the crystal possesses n such mirrors in all and the n-axis is included in a $\overline{2n}$-axis.

Theorems V and VI lead (Fig. 10) to the following groups: $\bar{4}2m$, $\bar{6}2m$.

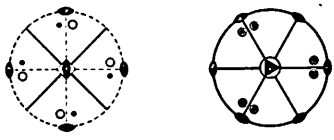

FIG. 10

Group $\bar{4}2m$ Group $\bar{6}2m$

Theorem VII: A $\overline{2n}$-axis is incompatible with either a mirror perpendicular to it, or the centre.

A $\bar{4}$-axis would lead to the group $4/m$ in both cases. A $\bar{6}$-axis and the centre would lead to $6/m$. (The inversion axis would become a rotation axis.) Adding a mirror perpendicular to a $\bar{6}$-axis has no meaning, since $\bar{6}$ already includes such a mirror ($\bar{6} = 3/m$).

Corollary: The only way in which a $\overline{2n}$-axis can combine is with n lateral 2-axes perpendicular to it and n mirrors through it.

Theorem VIII: In the absence of any singular axis, the only two combinations of rotation axes possible in crystals are: the octahedral axes (three 4-axes, four 3-axes, six 2-axes) and the tetrahedral axes (three 2-axes, four 3-axes).

The proof of theorem I is evident. Theorems II to VII are all proved in similar manner, by means of the stereographic projection. Select a face in general position, apply to it all the symmetry operations available in the given symmetry elements, then apply to it the available products of symmetry operations. The resulting equivalent faces will show, by their arrangement, the presence of additional symmetry elements and their characters (angles between

axes, polarity or homopolarity of axes and planes). In theorem III, Euler's theorem[14] is used to prove that no other 2-axis can exist without altering the period of the n-axis. In theorem IV, that no other mirror can exist is proved by remarking that the product of two reflections about intersecting mirrors is equal to a rotation about their intersection, through an angle equal to twice the angle between the mirrors. It is somewhat longer to prove theorem VIII. The first point is to show that if there is no singular axis, there must exist at least three rotation axes with the same period p, greater than 2. This proposition rests mainly on Euler's theorem. The rest of the proof is the same as that given in many text-books.[15]

THE POSSIBLE POINT-GROUPS

The problem is to combine, in all compatible manners, the following symmetry elements: axes (rotation axes: 1, 2, 4, 3, 6; inversion axes: $\bar{4}$, $\bar{6}$), centre ($\bar{1}$), mirror (m). Note that there is always an axis present, for any solid may be considered as having a 1-axis (this takes care of the asymmetrical crystals).

The method of derivation consists in establishing first all the axes and possible combinations of axes, then in combining them with the centre and mirrors. To exhaust all possibilities, the

[14]EULER'S THEOREM: Two rotations about intersecting axes are equivalent to a single rotation. A rotation through an angle α about OA, combined with a rotation through an angle β about OB, is equivalent to a single rotation through an angle γ about a third axis OC, to be found as follows. Let A and B (Fig. 11) be the poles of the two axes OA and OB on a sphere drawn around O. Draw two arcs of great circles AC and BC, making the angles $\alpha/2$ and $\beta/2$ with the arc AB. The point C, obtained at their intersection, is the pole of the axis OC, and the angle γ is equal to twice the angle ACB, or twice its supplement, according as the rotation about OC is taken clockwise or counter-clockwise. (The rotations about OA and OB are counter-clockwise.)

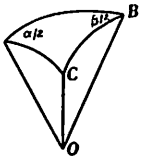

Fig. 11

Proof. Let m_a, m_b, m_c denote the reflections in the planes OBC, OCA, OAB. Then the rotations α about OA and β about OB are equivalent to two reflections each, namely $m_b m_c$ and $m_c m_a$. If these four reflections are applied in succession, the two reflections (m_c) in OAB cancel out, and the other two reflections ($m_b m_a$) are seen to be equivalent to a clockwise rotation, about OC, through twice the angle ACB.

[15]For instance: Friedel (1911 or 1926), Buttgenbach (1935).

dichotomous principle ("Either *this* . . . or *that* . . .") is followed throughout, as being the most satisfactory for the mind.

DERIVATION OF THE 32 POINT-GROUPS

Either there is a singular axis, or there is no singular axis.

I. **A Singular Axis.**—It is either a rotation axis n, or an inversion axis $\bar{2}n$.

A. The singular axis is a rotation axis n.—It is either uncombined, or combined.

1. Rotation axis uncombined. Groups: 1, 2, 4, 3, 6.
2. Rotation axis combined.—Either there is no other axis, or there is at least another axis.

(*a*) No other axis.—Two possibilities:

Centre present.—The axes 1 and 3 become $\bar{1}$ and $\bar{3}$, respectively; each even-fold axis acquires a mirror perpendicular to it (Th. II). No other mirror is possible, for, with the centre, it would create another even-fold rotation axis (Th. II).

Groups: $\bar{1}$, $\frac{2}{m}$, $\frac{4}{m}$, $\bar{3}$, $\frac{6}{m}$.

No centre.—Only mirrors through the singular n-axis[16] are possible, for no mirror can be oblique to it (Th. I), while a mirror perpendicular to it would require the centre, if n is even (Th. II), or transform it into an inversion axis, if $n = 3$ ($3/m$ equivalent to $\bar{6}$). Each n-axis acquires n mirrors passing through it, and no other (Th. IV).

Groups: m, $2mm$, $4mm$, $3m$, $6mm$.

(*b*) At least another axis. It must be a 2-axis perpendicular to the singular axis[16] (Th. I). Each n-axis acquires n such lateral 2-axes, and no other (Th. III).—Two possibilities:

No centre.—In this case, there can be no mirror.[17] For a mirror could only pass through the singular n-axis (proved above). It

[16]This may be taken to apply to the 1-axis as well, since such an axis is not defined in direction (any line is a 1-axis).

[17]Except if the singular n-axis is a 1-axis, when there is only one lateral 2-axis. This case has been considered above; it leads to the group $2mm$.

would have to contain a lateral 2-axis, or to bisect the angle between two lateral 2-axes, otherwise it would, by reflection, create additional 2-axes. Now if n is even, a mirror containing a lateral 2-axis would be perpendicular to another 2-axis, thus demanding the centre (Th. II), while a mirror bisecting two successive lateral 2-axes would require them to be alike, whereas they are of different kinds (Th. III). If $n = 3$, a mirror containing a 2-axis would (Th. VI) transform 3 into $\bar{6}$, while a mirror bisecting two successive 2-axes would be perpendicular to another 2-axis and create the centre (Th. II).

Groups: 2, 222, 422, 32, 622.

Centre present.—The 3-axis become $\bar{3}$; each even-fold axis acquires a mirror perpendicular to it (Th. II). No other mirror is possible, for, with the centre, it would create an additional even-fold axis (Th. II).

Groups: $\frac{2}{m}, \frac{2}{m}\frac{2}{m}\frac{2}{m}, \frac{4}{m}\frac{2}{m}\frac{2}{m}, \bar{3}\frac{2}{m}, \frac{6}{m}\frac{2}{m}\frac{2}{m}$.

B. The singular axis is an inversion axis $\overline{2n}$.—It is either uncombined, or combined.

1. Inversion axis uncombined. Groups: $\bar{4}$ and $\bar{6}$.
2. Inversion axis combined.

The only way in which a $\overline{2n}$-axis can combine is with n lateral 2-axes perpendicular to it, and n mirrors through it (Th. VII).

Groups: $\bar{4}2m$ and $\bar{6}2m$.

II. **No Singular Axis.**—The axes are either the tetrahedral axes or the octahedral axes (Th. VIII).

1. Tetrahedral axes: 2 3.—It is imperative to consider two cases: either the 2-axes are not included in $\bar{4}$-axes, or they are.
   (*a*) The 2-axes are not included in $\bar{4}$-axes.—Two possibilities:

No centre.—In this case, there can be no mirror. A mirror containing none of the 2-axes would, by reflection, create additional 2-axes. A mirror passed through one 2-axis must bisect the other two, which are alike, hence it would make the first 2-axis into a 4-axis (Th. VI). A mirror passed through two 2-axes is perpendicular to the third, hence would demand the centre (Th. II).

Group 2 3.

Centre present.—The 3-axes become $\bar{3}$-axes; each 2-axis acquires a mirror perpendicular to it (Th. II). No other mirror is possible, for, with the centre, it would create an additional even-fold axis (Th. II).

Group $\frac{2}{m}\,\bar{3}$.

(*b*) The 2-axes are included in $\bar{4}$-axes.—Only one possibility:

The centre is excluded by the $\bar{4}$-axes (Th. VII). Two 2-axes (included in $\bar{4}$-axes) are perpendicular to each $\bar{4}$-axis, hence they demand two mirrors alternating (Th. V). There are six mirrors in all, bisecting the 90° angles between the $\bar{4}$-axes. Any other mirror would, by reflection, create additional $\bar{4}$-axes.

Group $\bar{4}\,3\,m$.

2. Octahedral axes: 4 3 2.—The 2-axes cannot be included in $\bar{4}$-axes because each 2-axis is perpendicular to a plane containing one 4-axis, one 2-axis, two 3-axes, and a $\bar{4}$-axis cannot be perpendicular to such a combination. Two possibilities:

No centre.—In this case, there can be no mirror. A mirror containing none of the 4-axes would, by reflection, create additional 4-axes. A mirror passed through one 4-axis must bisect the other two, which are alike, and thus be perpendicular to a 2-axis, thereby requiring the centre (Th. II). A mirror passed through two 4-axes is perpendicular to the third, hence would demand the centre (Th. II).

Group 4 3 2.

Centre present.—The 3-axes become $\bar{3}$-axes; each even-fold rotation axis acquires a mirror perpendicular to it (Th. II). No other mirror is possible, for, with the centre, it would create an additional even-fold rotation axis (Th. II).

Group $\frac{4}{m}\bar{3}\frac{2}{m}$.

CONCLUSIONS

The results of the preceding derivation are presented in Table I. Notice that, on the first horizontal row, $\bar{4}$ and $\bar{6}$ are placed after 2 and 3 respectively. This arrangement emphasizes the fact that a

2-axis may exist as such or as part of a $\bar{4}$-axis; likewise, a 3-axis may be alone or included in a 6-axis.

The derivation, although based on simple mathematical prerequisites, skips no single step. It leads to the international symmetry symbols. It has other advantages, which can be gathered on inspection of Table I, namely: (*a*) The 32 groups are established with a minimum of duplication (only two are found twice[18]). (*b*) They are derived in such a sequence as to fall naturally into the six systems, the seven lattice symmetries and the eleven Laue symmetries. (*c*) The parallelism of the two cases where the singular axis is an inversion axis with an even period ($\bar{4}$ and $\bar{4}2m$ on the one hand, $\bar{6}$ and $\bar{6}2m$ on the other) is well brought out. (*d*) The three *orders* of merohedry (hemi, tetarto, and ogdo) and the three *kinds* of hemihedry (para, anti, and holoaxial) are clearly shown.[19]

TABLE I

THE 32 POINT-GROUPS

1	2	$\bar{4}$	4	3	$\bar{6}$	6	2 3
$\bar{1}$	$\frac{2}{m}$		$\frac{4}{m}$	$\bar{3}$		$\frac{6}{m}$	$\frac{2}{m}\bar{3}$
m	2 m m	$\bar{4}$ 2 m	4 m m	3 m	$\bar{6}$ 2 m	6 m m	4 3 m
2	2 2 2		4 2 2	3 2		6 2 2	4 3 2
$\frac{2}{m}$	$\frac{2}{m}\frac{2}{m}\frac{2}{m}$		$\frac{4}{m}\frac{2}{m}\frac{2}{m}$	$\bar{3}\frac{2}{m}$		$\frac{6}{m}\frac{2}{m}\frac{2}{m}$	$\frac{4}{m}\bar{3}\frac{2}{m}$

ACKNOWLEDGMENTS

I am indebted to Professor H. S. M. Coxeter (University of Toronto) for the idea of converting a Cartesian axial cross into

[18]Namely 2 and $2/m$. The reason for this is that a 1-axis, combined with a 2-axis, is equivalent to a singular 2-axis alone.

[19]All hemihedral point-groups in the second row are parahemihedries, all the antihemihedries appear in the third row, etc. Merohedry (or merosymmetry) now divorced from the erroneous notions long associated with it (so-called "deficient elements of symmetry") has proved to be a most fruitful concept in crystallography (witness the French theory of twinning, Friedel, 1926).

another, similarly oriented, by two reflections instead of three rotations, as well as for the proof of Euler's theorem (given in footnote 14).

My thanks are also due to Professor S. J. Shand (Columbia University) for a critical reading of the manuscript, and to my colleague Professor Franco Rasetti (Université Laval) for many enlightening discussions.

APPENDIX

For the reader's convenience a tabulation of the 32 crystal classes (Table II) is appended.[20] It gives the concordance between the international symbols, Groth's names of the crystal classes, and the French classification of symmetries into holohedries and merohedries. It indicates the *order of the group* (number of faces in the general form, also called *symmetry number*) and shows the relationships with systems and lattice modes.

The classification of symmetries into holo- and merohedries is especially useful in the study of twinning. The fundamental *fact* is that a crystal may have the same symmetry as its lattice (case of *holohedry*) or have a lower symmetry than its lattice (case of *merohedry*). The nomenclature of merohedries distinguishes three orders of merohedry: *hemihedry*, *tetartohedry*, *ogdohedry*. It also discriminates between three kinds of hemihedry: *holoaxial* (with all the axes of the holohedry), *para-* (with the centre, hence parallel faces), *anti-* (without centre). The subdivision into three kinds rests on the existence of three symmetry elements of order 2, namely: the 2-axis, the centre, the mirror. A tetartohedry being the hemihedry of a hemihedry, the same designations apply to tetartohedries. There is only one case of ogdohedry.

Whenever there are two or more hemihedries or tetartohedries of the same kind, I would propose to distinguish them by stating the polarity of the principal symmetry axis (*polar*, *homopolar*), or its period (*trigyre*, *hexagyre*), or both if necessary. The polarity suffices to discriminate between the two antihemihedries and the two tetartohedries of the tetragonal system. In the hexagonal system (*C*-lattice) two antihemihedries are likewise differentiated as polar and homopolar; two parahemihedries are distinguished as trigyre and hexagyre; out of three antitetartohedries one is homopolar, while two are polar; the latter are separated into trigyre and hexagyre (they are the only two cases where two adjectives are required). The slight changes proposed to the French nomenclature bring about an appreciable simplification. In its suggested form, the terminology is systematic and straightforward; it uses a minimum of words, all of which are well known.

For most purposes, however, the international symbols should suffice. They can be spoken as easily as they can be written. It is much more con-

[20] At the suggestion of Professor M. A. Peacock.

TABLE II

CONCORDANCE BETWEEN THE INTERNATIONAL SYMMETRY SYMBOLS AND OTHER CRYSTAL-CLASS DESIGNATIONS

Crystal system and possible lattice modes		French classification of symmetries (modified after Friedel)		International symbols			Crystal class names (Rogers, modified after Groth)	Order of the group
Triclinic		Hemi-		1			Pedial	1
P		Holo-		$\bar{1}$			Pinakoidal	2
Monoclinic		Antihemi-		*m*			Domatic	2
P, *C*(*A*)		Holoaxial hemi-		2			Sphenoidal	2
		Holo-		2/*m*			Prismatic	4
Orthorhombic		Antihemi-		*m*	*m*	2	Rhombic pyramidal	4
		Holaxial hemi-		2	2	2	Rhombic disphenoidal	4
P, *C*(*A*, *B*), *I*, *F*		Holo-		2/*m*	2/*m*	2/*m*	Rhombic dipyramidal	8
Tetragonal		Tetarto-	homopolar	$\bar{4}$			Tetragonal disphenoidal	4
			polar	4			Tetragonal pyramidal	4
		Parahemi-		4/*m*			Tetragonal dipyramidal	8
		Antihemi-	homopolar	$\bar{4}$	2	*m*	Tetragonal scalenohedral	8
P, *C*			polar	4	*m*	*m*	Ditetragonal pyramidal	8
		Holaxial hemi-		4	2	2	Tetragonal trapezohedral	8
		Holo-		4/*m*	2/*m*	2/*m*	Ditetragonal dipyramidal	16
Hexagonal	*R*, *C*	Tetarto-	Ogdo-	3			Trigonal pyramidal	3
		Parahemi-	Paratetarto-	$\bar{3}$			Rhombohedral	6
		Antihemi-	Antitetarto- (polar trigyre)	3	*m*		Ditrigonal pyramidal	6
		Holoaxial hemi-	Holoaxial tetarto-	3	2		Trigonal trapezohedral	6
		Holo-	Parahemi- (trigyre)	$\bar{3}$	2/*m*		Hexagonal scalenohedral	12
	C		Antitetarto- {homopolar	$\bar{6}$			Trigonal dipyramidal	6
			polar hexagyre	6			Hexagonal pyramidal	6
			Parahemi- (hexagyre)	6/*m*			Hexagonal dipyramidal	12
			Antihemi- {homopolar	$\bar{6}$	*m*	2	Ditrigonal dipyramidal	12
			polar	6	*m*	*m*	Dihexagonal pyramidal	12
			Holoaxial hemi-	6	2	2	Hexagonal trapezohedral	12
			Holo-	6/*m*	2/*m*	2/*m*	Dihexagonal dipyramidal	24
Isometric (cubic)		Tetarto		2	3		Tetartoidal	12
P, *I*, *F*		Parahemi-		2/*m*	$\bar{3}$		Diploidal	24
		Antihemi-		$\bar{4}$	3	*m*	Hextetrahedral	24
		Holoaxial hemi-		4	3	2	Gyroidal	24
		Holo-		4/*m*	$\bar{3}$	2/*m*	Hexoctahedral	48

The dash after each name in the second column may be taken, according to personal preferences, to stand for the time-honoured "hedry" or "hedrism," or for "symmetry" as recently proposed by Rogers (1939).

venient, it seems to me, to refer to "class $\bar{6}$" than to speak of the "trigonal dipyramidal class" or the "homopolar antitetartohedry of the hexagonal lattice." To say that scheelite belongs to class $4/m$ ("four over *m*") is just as elegant as to say that its chemical composition is $CaWO_4$ ("*c-a*-double *u-o*-four"). The space-group symbols (*Pbnm*, *Amam*, etc.) can likewise be spoken, and they are—universally. The effort of the man who devised 230 names for the 230 space-groups is to be regarded as a contribution to philology rather than crystallography.

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RECROSSING AXIAL PLANE DISPERSION IN GOETHITE

By E. W. NUFFIELD and M. A. PEACOCK
University of Toronto

The monohydrate of ferric oxide, $Fe_2O_3.H_2O$ or FeO.OH, exists in two structurally distinct forms, α-FeO.OH and γ-FeO.OH, both of which are known as crystallized minerals. These were undistinguished under the name goethite in Dana (1892); now the natural α-FeO.OH is named goethite *sensu stricto*, while the natural γ-FeO.OH is called lepidocrocite. According to the latest crystallographic description (Peacock, 1942) crystals of goethite, in the above sense, are orthorhombic (*Pbnm*), with

$$a : b : c = 0.4616 : 1 : 0.3034$$

habit, short prismatic to acicular parallel to [001]; cleavage (010), perfect.[1] Crystals of lepidocrocite are also orthorhombic (*Amam*), with

$$a : b : c = 0.3088 : 1 : 0.2448$$

habit, tabular to platy parallel to (010); cleavage (010), perfect and very easy. The minerals are at once distinguished by *x*-ray powder photographs which have shown furthermore that most of the materials named "limonite" are structurally the same as goethite.

The uncertainties that formerly surrounded the hydrated ferric oxide minerals led to repeated optical studies which revealed remarkable properties in goethite and eventually indicated the distinction between goethite and lepidocrocite. The first important observations were made by Palla (1885), who noted extreme dispersion of the optic axes ($2E$ near 0° for red, about 50° for blue) about the bisectrix normal to the (010) cleavage. Palla gave the optic sign as probably positive with the optic plane apparently parallel to (001); he suggested an analogy with brookite, the famous case of crossed axial plane dispersion, but was unable to decide whether this effect actually took place in goethite. These incomplete and partly erroneous observations were the latest available to Dana (1892).

[1] In the structural setting the directions of the crystallographic axes, *a*, *b*, *c*, are the same as they were in the classical setting.

A more detailed study of the optics of goethite was made by Pelikan (1894) using thin sections cut parallel to the three pinakoids of Cornish crystals. These showed moderate pleochroism, *a* dark brown, *b* yellow brown, *c* light orange yellow. The (010) section showed traces of a weaker cleavage, taken to be (100), and the emergence of the negative acute bisectrix. Crossed axial dispersion was clearly observed, with the optic axial plane parallel to (100) for red, parallel to (001) for green, and $2E$ 58°31′ (red), 67°42′ (yellow). One plate showed $2E$ 36°46′ (yellow). The mean refractive index was estimated about 2.5, the birefringence about 0.134.

Mügge (1916) confirmed the negative optic sign of goethite and the crossed axial dispersion, with the axial plane (100) for red, (001) for yellow at the ordinary temperature. The microspectroscope showed a dark band in the red at about 605 mμ, probably the wave-length at which the mineral is uniaxial; with increasing temperature this band moved out beyond the violet. For the yellow mercury lines 577 and 579 mμ $2E$ was 83°21′ in the plane (001) at 12°C., 0° at 59°C., 96°11′ in the plane (100) at 102.5°C. Thus Mügge found that goethite displayed crossed axial dispersion at constant wave-length and varying temperature, the rare effect best known in gypsum.

Further valuable optical data were contributed by Posnjak and Merwin (1919) in a detailed study of the hydrated ferric oxides. These authors found that goethite is optically negative with $a = b$, $\gamma = c$ for red, $a = b$, $\gamma = a$ for blue; uniaxial ($\beta = \gamma$) usually at 610 to 620 mμ; $2E$ about 80° at 600 mμ, but variable in different specimens. The indices of refraction were measured by immersion in melts: for Na-light, α 2.260, β 2.393, γ 2.398 (all $\pm$ 0.005), but variable in different specimens; for Li-light (Larsen), α 2.21, β and γ 2.33-2.35. The absorption of goethite was found to increase abruptly toward the blue, near 550 mμ.

With the remarkable properties of goethite apparently rather fully described we examined some (010) cleavage plates mainly to become familiar with the unusual effects of crossed axial dispersion with varying wave-length and temperature. We quickly confirmed the negative character of the acute bisectrix normal to (010) and the crossing of the axial plane from (001) for white and yellow to (100) for red. Blue light was strongly absorbed, as noted by Posnjak and Merwin, but in violet light we were pleasantly surprised to

obtain good transmission and a clear interference figure showing the optic axial plane again parallel to (100), as in the red. Thus the axial plane crossed from (100) to (001) and recrossed from (001) to (100) in passing from red to violet. As this effect of *recrossing axial plane dispersion* has apparently not been observed before it was examined more closely both at the ordinary temperature and at higher and lower temperatures.

EXPERIMENTAL ARRANGEMENTS

Our observations were limited to determinations of the optical orientation and the apparent optic axial angle shown by (010) cleavage plates from Cornish crystals[2] in convergent light of various colours and at various temperatures. Owing to the strong brown body-colour of the mineral satisfactory interference figures were obtained only in thin plates (about 0.02-0.05 mm.) mounted in balsam and examined under the microscope. Such plates show the

TABLE 1

WRATTEN FILTERS AND APPROXIMATE MEAN WAVE-LENGTHS OF TRANSMITTED LIGHT

Filter No.	Colour	Wave-length
36	Violet	420 $m\mu$
35	Bluish violet	435
49	Blue	460
75	Greenish blue	490
62	Bright green	540
73	Olive-green	570
25	Light red	640
29	Medium red	660
70	Dark red	680

brushes of the acute bisectrix figures but no lemniscates. In the diagonal position the sharpness of the brushes varies somewhat with the colour of light, permitting only moderately accurate measurements of the apparent optic axial angle with the aid of a calibrated ocular. The optic sign was determined with the quartz wedge on a substantially thicker plate showing one sharp lemniscate in Na-light.

[2]Similar to those recently measured and figured (Peacock, 1942).

The prism spectroscope at our disposal did not give sufficiently strong monochromatic light for our purpose, and therefore we were obliged to use the approximately monochromatic light given by Wratten filters in conjunction with a white source. The filters[3] used, and the approximate mean wave-lengths of the transmitted light, are given in Table 1. For yellow light the sodium vapour arc (590 mμ) was used.

Controlled temperatures of 0-60°C. were obtained with the help of a round flat-bottomed glass dish, 10 cm. wide and 1 cm. deep, containing water which completely covered the preparation and the nose of the objective. This simple arrangement did not increase the distance from the converging lens to the objective enough to impair the optic figures. A temperature of 0°C. was got by placing ice and some salt in the dish; the higher temperatures were obtained by adding hot water in various proportions, stirring the bath, and measuring the temperature at the time of observation. In this way temperatures sufficiently steady for our purpose were obtained.

RESULTS

The measured values of the optic axial half-angle in air (E) for the wave-lengths 420-680 mμ and the temperatures 0°, 25°, 43°C., are listed in Table 2 and plotted in Fig. 1. The optic sign is nega-

TABLE 2

GOETHITE: OPTIC AXIAL ANGLE IN AIR (E) AT VARIOUS WAVE-LENGTHS AND TEMPERATURES

λ	0°	25°	43°C.
420 mμ	−27½°	−36°	−25°
435	−25	−33	−27½
460	+19½*	−12*	−19½*
490	+30½*	+ 2*	−25*
540	+49½	+53	+26
570	+51	+33	+23½
590 (Na)	+42½	+27½	+11
640	+27½	− 9½	−23½
660	+11	−19½	−30½
680	−25	−33	−30½

*Optic figure indefinite.

[3]Kindly made available by Miss E. J. Allin, Department of Physics, University of Toronto.

tive throughout; $-E$, plotted below the zero line in Fig. 1, denotes an apparent angle in the plane (100), as in the lower insets; $+E$, plotted above the zero line, is an apparent angle in the plane (001), as in the upper inset.

Except for some irregularities, mainly in the blue where the figure is obscure, the three sets of points are tolerably represented by smooth curves which rise from a negative value (in the foregoing

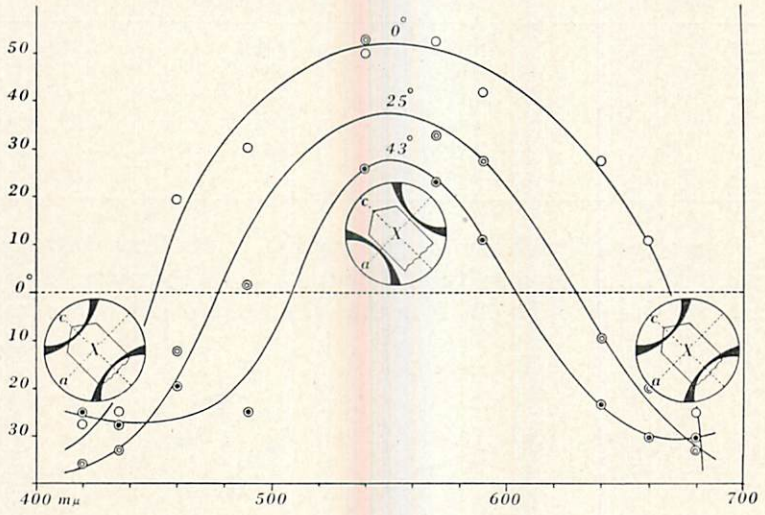

FIG. 1.—Goethite. Variation of the optic axial half-angle in air (E) with crossing and recrossing of the optic axial plane at varying wave-lengths and three temperatures.

sense) in the violet, cross the zero line steeply, rise to positive maxima in the green, recross the zero line, and fall to negative values in the red. The moderate range of temperature employed gives substantial displacements in the E-curves, and one might predict that for temperatures much below 0°, or above 43°, the curves would fail to cross the zero line in visible light and therefore no crossing of the axial plane would take place.

The approximate wave-lengths at which E is zero, and the mineral is momentarily uniaxial, is given by the curves as follows: at 0°, 450 and 669 mμ; at 25°, 478 and 630 mμ; at 43°, 509 and 608 mμ. Posnjak and Merwin (1919) found the uniaxial condition at 610 to 620 mμ, which would correspond to a temperature of about 35°C.

on our graph. While this (95°F.) is an improbable room temperature, even for Washington, D.C., a powerful light source and the converging lens might have heated the preparation to this extent.

TABLE 3

GOETHITE: OPTICAL AXIAL ANGLE IN AIR (E) AT 590 mμ AND VARYING TEMPERATURES

Temperature	E	Temperature	E
0°C.	+42½°	42½C°.	+ 9½°
5	+33	44	+ 5
25	+27½	46	0
28½	+25	51½	−11
34	+22½	55	−17
40	+14½	60	−19½

The observed variation of the angle E in Na-light (590 mμ), from 0-60°C., is given in Table 3 and Fig. 2. The points lie on a curve which falls from 42½°E in the orientation of the upper inset

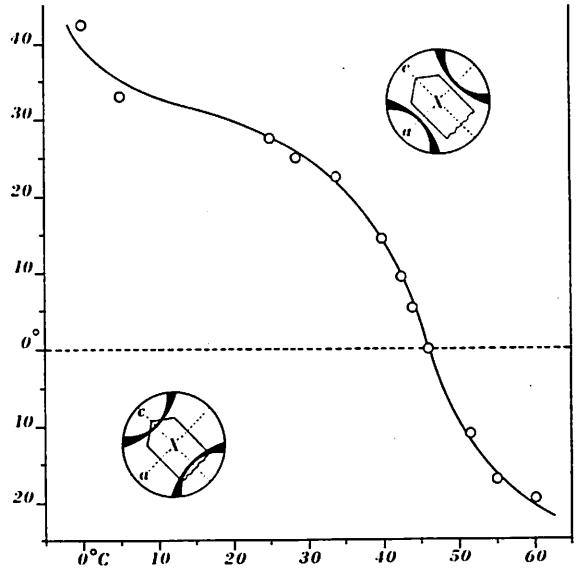

FIG. 2. Goethite. Variation of the optic axial half-angle in air (E) with crossing of the optic axial plane with varying temperature at 590 mμ.

at 0°C., through 0°E (uniaxial) at 46°C., to 19½°E in the orientation of the lower inset at 60°C.

DISCUSSION

Since the optic axial angle is a function of the principal indices of refraction, variation of the optic axial angle and change of optic orientation with change of wave-length and change of temperature may be best explained with reference to the variation of the prin-

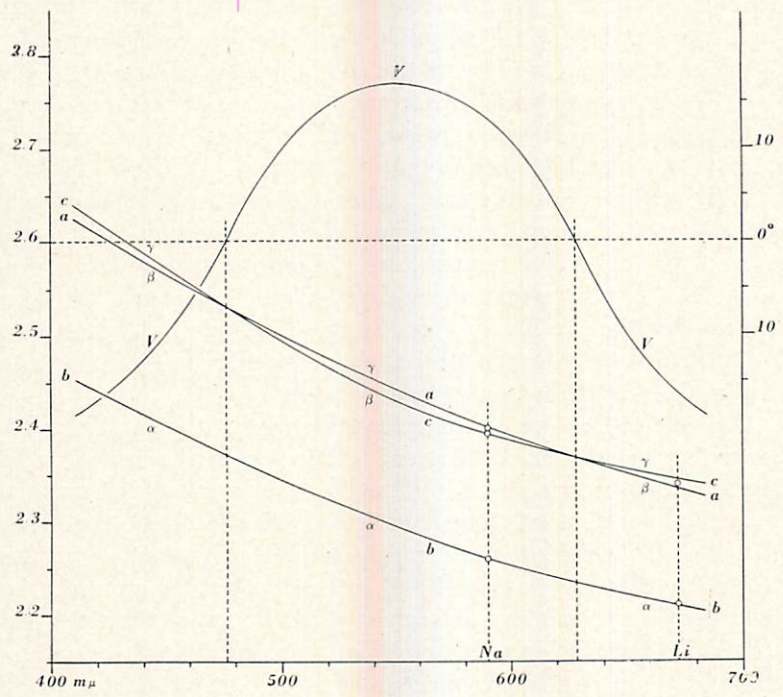

FIG. 3.—Goethite. Assumed curves for the principal refractive indices explaining the recrossing axial plane dispersion at constant temperature.

cipal indices of refraction. The values of E, V, α, β, γ, are related by the familiar formulae:

$$\text{Sin } E = \beta . \text{ Sin } V; \quad \text{Cos}^2 V_\alpha = \gamma^2(\beta^2 - \alpha^2)/\beta^2(\gamma^2 - \alpha^2)$$

Data for an actual quantitative presentation of the relations in goethite are not available, but Merwin's values for α, β, γ, in Na-

light and Larsen's values in Li-light suffice to construct a diagram (Fig. 3) showing the mode of variation of α, β, γ, with V. The three curves rising from the red to the violet represent the refractive indices of light vibrating parallel to the crystallographic axes, a, b, c. The lowest curve, b, gives the refractive index α throughout its length; the curves, a and c, cross and recross at the uniaxial positions; in the red we have $\alpha = b$, $\beta = a$, $\gamma = c$, giving the optic axial plane (100); in the green $\alpha = b$, $\beta = c$, $\gamma = a$, giving the optic axial plane (001); in the violet the relations are the same as in the red. The curve for the optic axial angle V corresponds to the curves for α, β, γ, and roughly represents the conditions at 25°C.[4]

At lower temperatures the curves for α, β, γ, will be moved upwards and the points of crossing will be moved outwards until, presumably, a temperature is reached where $\alpha = b$, $\beta = c$, $\gamma = a$, throughout the visible range; at higher temperatures the curves will be depressed, the points of crossing will approach one another, and we may expect that a temperature will be reached where $\alpha = b$, $\beta = a$, $\gamma = c$, throughout the visible range. The variation of E with temperature at 590 mμ (Fig. 2) may be similarly explained by simultaneous and unequal displacement of the curves for a, b, c, with crossing of the a- and c-curves at 46°C.

The inferred course of the refractive index curves conforms to the known conditions underlying dispersion with crossed axial planes, namely near equality of β and γ, or of α and β, and unequal dispersion of the nearly equal indices, with the result that they become equal at certain wave-lengths and temperatures. A further condition stated by Tutton (1906) to be essential for crossed axial plane dispersion, namely extremely small double refraction, certainly does not hold in goethite, or in brookite, since $\gamma - \alpha$ is unusually large in both these minerals.

Thus goethite may be counted among the relatively few crystalline substances that show crossed axial plane dispersion with varying wave-length and varying temperature.[5] The effect with varying wave-length is more pronounced than in brookite, while the tempera-

[4] In the drawing the maximum values of $\gamma - \beta$, and consequently of V, are somewhat greater than those required by the measured values of E.

[5] Tutton (1911, p. 784) reviews the known examples of this phenomenon in a detailed treatment of the subject.

ture effect is notably stronger than in gypsum and comparable to that described in saccharin (Brugnatelli, 1897). Furthermore the section normal to the acute bisectrix is more favourably placed in goethite than in the two other minerals mentioned, so that these effects, with the added interest of the second crossing of the axial plane, can be easily observed without the aid of specially cut sections.

If the remarkable optical properties of goethite should be further examined, it would be desirable to measure the principal refractive indices accurately on oriented prisms in strong monochromatic light. The dispersion curves thus obtained would probably resolve a point on which we are doubtful, namely the nature of the absorption in the blue. In this region we obtained a nearly dark field, obscure figures, and erratic values for E, indicating partial rather than complete absorption. It is possible that strictly monochromatic light would reveal a true absorption band in this region, in which case we would expect the dispersion curves to be interrupted. While this would not invalidate the second crossing of the axial plane in the violet, the curves for α, β, γ, V, E, would not pass smoothly through the critical wave-length, as we have represented them in first approximation.

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STUDIES OF MINERAL SULPHO-SALTS:

VI—AIKINITE

By M. A. Peacock
University of Toronto

The rare ore mineral aikinite (*needle-ore, patrinite*), from Berezovsk in the Urals, was already known to Mohs and Haüy and its composition ($CuPbBiS_3$) was early established by Frick (1834, in Dana, 1892). On the poorly developed unterminated needle-like crystals, Miers (1889) obtained the axial ratio $a : b = 0.9719 : 1$, showing no definite relation to the ratios of bournonite ($CuPbSbS_3$) with which aikinite has always been classed on the basis of chemical analogy. More recently Frondel (1941) noted that *x*-ray powder photographs of aikinite differ markedly from those of the chemically analogous minerals bournonite and seligmannite ($CuPbAsS_3$) and that, therefore, aikinite is probably not to be grouped with these species. In his valuable *Tables*, Harcourt (1942) gives *x*-ray powder spacings and intensities for aikinite, and he also observes (p. 108) that the pattern of aikinite is quite different from those of bournonite and seligmannite. Aikinite has been reported from France, Germany, Tasmania, and the United States (Hintze, 1904, p. 1138), but at least in some cases the identification is dubious. Latterly the mineral has again been reported, by Anderson (1940), from the Lava Creek district, Idaho.

Some years ago, Dr. H. Berman kindly lent me a typical specimen of aikinite from Berezovsk (patrinite, Harvard Mineralogical Museum, 82490) for further study.[1] The specimen shows massive aikinite with the characteristic dark metallic lustre, coppery tarnish, and occasional coating of verdigris, embedded in vein quartz. On clean fragments two measurements of the specific gravity gave 7.08 (on 28 mg.), 7.07 (on 14 mg.). The previous values 6.757 (Frick), 6.1 (Chapman), given in Dana (1892) appear to be too low and in view of the constancy of the composition of the mineral the suggested variation of specific gravity is probably unreal.

[1]The results of this work were privately communicated to Dr. Berman (Sept. 5, 1940) to supplement the description of aikinite in the forthcoming revision of Dana's *System*.

In places aikinite forms distinct but unterminated prismatic to needle-like crystals, channelled lengthwise and embedded in the gangue. This material yielded a crystal fragment suitable for rotation and Weissenberg x-ray photographs (Figs. 1, 2) with the needle-axis as the axis of rotation. These photographs confirmed the orthorhombic symmetry previously assumed for aikinite and yielded the cell dimensions given below. The reflections in /hk0/ and /hk1/ conform to the conditions:

(hkl) present in all orders	(P)
(0kl) present only with $(k + l)$ even	(n)
(h0l) present only with h even	(a)
(hk0) present in all orders	(m or 2)

The space-group is thus $D_{2h}^{16} = Pnam$ or $C_{2v}^{2} = Pna2$. If aikinite is holohedral it provides another example of the space-group D_{2h}^{16} which recurs with such astonishing frequency, especially among the sulpho-salts.

In keeping with the striking contrast between the needle-like habit of aikinite and the thick-tabular to pseudo-cubic habit of bournonite, and the dissimilarity of their x-ray powder photographs, the two minerals are unlike in symmetry and cell dimensions. Aikinite and bismuthinite (Bi_2S_3), however, show unexpected similarities, especially when the horizontal axes of bismuthinite are interchanged (in brackets):

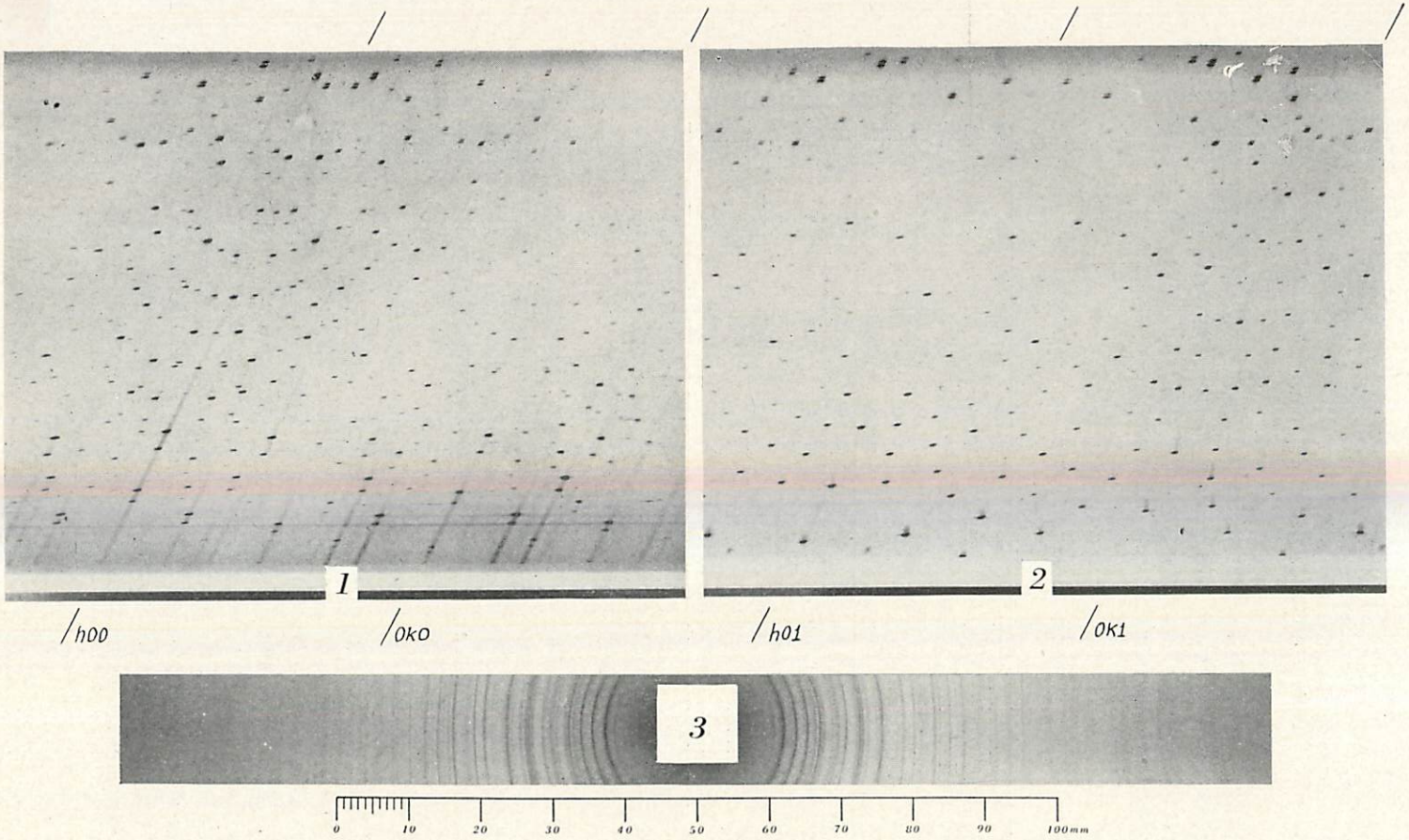
	AIKINITE (PEACOCK)	BISMUTHINITE	(HOFMANN, 1933)
Space-group	*Pnam* or *Pna*2	*Pbnm*	(*Pnam*)
a_0	11.30 Å	11.13 Å	(11.27 Å)
b_0	11.64	11.27	(11.13)
c_0	4.00	3.97	(3.97)
Cell content	4[CuPbBiS$_3$]	4[Bi_2S_3]	

With different numbers of atoms in their unit cells aikinite and bismuthinite cannot, of course, be isostructural; at the same time the above comparison can hardly be without structural significance, even though lengths of about 4 Å and 11 Å occur frequently among the cell dimensions of the sulpho-salts.

The cell sides of aikinite give the axial ratios:

$$a_0 : b_0 : c_0 = 0.9708 : 1 : 0.3436$$

in which the ratio $a_0 : b_0$ agrees well with the geometrical ratio $a : b = 0.9719 : 1$, given by the angle $(110):(1\bar{1}0) = 88°22'$, which



FIGS. 1, 2.—Aikinite. Weissenberg photographs of a crystal rotating about the needle-axis [001]; unfiltered Cu-radiation; camera radius, $360/4\pi$ mm.; full-size reproductions. FIG. 1.—Resolution of the zero layer-line /*hk*0/. FIG. 2.—Resolution of the first layer-line /*hk*1/.

FIG. 3.—Aikinite. *X*-ray powder photograph with Cu-radiation (Ni-filter); camera radius, $360/4\pi$ mm. (1 mm. on film = $1°\theta$); full-size reproduction of contact print.

was obtained by Miers (1889) from "observations (which are merely approximate) . . . made partly upon crystal fragments and partly upon the impressions of needles in the quartz, which have a much brighter surface than the needles themselves."

TABLE 1

AIKINITE: ANALYSES AND CELL CONTENTS

		1	2	3	4	5	A
Analyses	Cu	11.79	10.59	10.97	11.11	10.90	11.04
	Ni	.....	.....	0.36	.....	.....	.....
	Pb	35.69	36.05	36.31	35.15	36.01	35.98
	Bi	34.62	36.45	34.87	36.25	36.20	36.28
	Au	.....	.....	0.09	.....	.....	.....
	S	16.05	16.61	16.50	16.56	16.60	16.70
		98.15	99.70	99.10	99.07	99.71	100.00
Atoms in unit cell	Cu	4.27	3.77	3.94	3.99	3.88	4
	Ni	.....	.....	0.14	.....	.....	..
	Pb	3.96	3.94	4.00	3.87	3.94	4
	Bi	3.81	3.95	3.81	3.96	3.92	4
	S	11.52	11.72	11.74	11.78	11.73	12

Analyses 1-5, Berezovsk, Ekaterinburg, Urals. 1, 2. Anal. Frick (1834, in Dana, 1892). 3. Anal. Hermann (1858, in Dana, 1892). 4, 5. Anal. Guillemain (1898). A. Percentage composition of $CuPbBiS_3$.

Table 1 gives the available analyses of aikinite, excluding only the early discordant analysis of Chapman (1847, in Dana, 1892), and the corresponding numbers of atoms in the unit cell calculated from the cell volume and the higher measured specific gravity (7.08). The cell content is clearly:

$$Cu_4Pb_4Bi_4S_{12} = 4[CuPbBiS_3] = 2[Cu_2S.2PbS.Bi_2S_3]$$

which gives the calculated specific gravity 7.22.

This cell content is compatible with the holohedral space-group D_{2h}^{16} in which there are only 4-fold and 8-fold equivalent positions.

Aikinite gives a distinctive x-ray powder pattern which is reproduced without reduction in Fig. 3 to aid in the future identification of the mineral. The measured spacings and intensities agree with those given by Harcourt (1942) for aikinite from Berezovsk, except for differences of detail due to differences of apparatus and mode of measurement. Table 2 gives the x-ray powder data for aikinite in

TABLE 2

AIKINITE: $Cu_2S.2PbS.Bi_2S_3$

Orthorhombic, *Pnam*; $a_0 = 11.30$, $b_0 = 11.64$, $c_0 = 4.00$ Å; $Z = 2$

I	θ(Cu)	*d*(meas.)	(*hkl*)	*d*(calc.)	*I*	θ(Cu)	*d*(meas.)
3	10.9°	4.07 Å	(220)	4.05 Å	½	31.1	1.488
½	11.75	3.77	(011)	3.78	1	31.4	1.475
10	12.1	3.67	(130)	3.67	3	33.15	1.406
			(111)	3.59	1	33.85	1.380
6	12.4	3.58	(310)	3.59	1	34.6	1.354
8	14.0	3.18	(121)	3.17	2	35.3	1.330
			(040)	2.91	½	36.2	1.302
7	15.5	2.88	(221)	2.85	1	37.2	1.271
1	16.3	2.74	(410)	2.75	1	39.2	1.216
			(131)	2.70	1	40.9	1.174
2	16.65	2.68	(330)	2.70	1	41.6	1.158
			(311)	2.67	1	43.2	1.123
5	17.3	2.58	(240)	2.59	1	45.2	1.083
½	17.5	2.56	(420)	2.54	1	48.9	1.020
½	17.8	2.51	(231)	2.50	1	51.0	0.989
*(1	19.0	2.36)	....	....	1	52.0	0.975
2	19.8	2.27	(150)	2.28			
1	20.7	2.17	(241)	2.17			
2	20.9	2.15	(250)	2.15			
			(421)	2.15			
2	22.35	2.02	(440)	2.03			
			(051)	2.01			
4	22.8	1.984	(431)	1.983			
			(151)	1.981			
3	23.25	1.947	(530)	1.953			
			(112)	1.942			
2	24.1	1.883	(202)	1.885			
			(600)	1.883			
½	25.2	1.805	(441)	1.808			
3	25.8	1.766	(351)	1.775			
			(132)	1.756			
½	27.8	1.648	(042)	1.648			
			(170)	1.645			
3	28.85	1.593	(270)	1.595			
3	30.3	1.524	(370)	1.521			

*Strongest line of gold.

the fuller form proposed in a recent paper (1941). In preparing this table all the possible spacings were calculated down to $d = 1.510$ Å, and thus the pattern is rigorously indexed as far as $\theta = 30°$. In this

way the pattern is verified and intensity data are obtained which may later be of use in determining the crystal structure.

One line of the powder pattern ($d = 2.36$, $I = 1$), also given by Harcourt with the same spacing and intensity, does not correspond to a possible set of planes in aikinite. It does, however, agree with the strongest line in the pattern of gold ($d = 2.36$, $I = 9.0$, Harcourt) which is regularly associated with aikinite and has been reported in the form of included grains, by Koksharov (1858, in Hintze, 1904, p. 1138). Unfortunately the single available specimen did not permit the preparation of a polished section to verify the presence of included gold in our material.

It remains to mention some observations on material recently described as aikinite by Anderson (1940), from the Lava Creek district, Idaho, and kindly sent to me for examination by Dr. Anderson. The needle-like lead-grey mineral in the material submitted gave an x-ray powder pattern showing no resemblance to that of aikinite. It does, however, resemble Harcourt's pattern for schapbachite ($Ag_2S.PbS.Bi_2S_3$); but since the patterns are not identical, and schapbachite itself requires further investigation, the identity of the mineral from Idaho is not clearly established.

SUMMARY

Aikinite from Berezovsk, Urals, with specific gravity 7.08, 7.07, has an orthorhombic unit cell with space-group *Pnam* (or *Pna*2); $a_0 = 11.30$, $b_0 = 11.64$, $c_0 = 4.00$ Å, containing 4[$CuPbBiS_3$]. The powder pattern is reproduced and indexed to $\theta = 30°$; it shows one foreign line, apparently due to included gold. Aikinite is not isostructural with bournonite and seligmannite, but the space-group and cell dimensions show a relation to bismuthinite.

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NOTES ON THE IRON ORES OF STEEPROCK LAKE ONTARIO[1]

By F. G. Smith
Copper Cliff, Ontario

In the winter of 1938 drilling through the ice on Steeprock Lake in the Atikokan area, Rainy River district, revealed high grade iron ore beneath the lake. This discovery led to a re-examination of the area, particularly by Moore (1940), Bartley (1940), and Tanton (1941), who describe the general geology of the region and the nature and extent of the iron ore, so far as it was known, and discuss the origin of the deposit. In these reports the iron ore is generally called hematite; Tanton also mentions specularite, limonite, goethite, jaspilite, and ferrodolomite.

During the summer of 1941 the writer assisted Dr. T. L. Tanton in mapping part of the area around Steeprock Lake for the Geological Survey of Canada. Special consideration was given to the detailed structure in the immediate vicinity of the iron ore-bodies underlying the lake, and the opportunity was taken to collect specimens of the ore with a view to determining the minerals present and the conditions under which they were formed.

The material collected includes float ore from the south shore of Steeprock Lake and from Floatore Island, south of the *A* ore-body; fragments from vertical and inclined drill-holes in the *A* and *B* ore-bodies, supplied by the Steeprock Iron Mines, Ltd.; and samples of the carbonate and magnetite iron formations near the East Arm of the lake. This material was studied with the help of thin sections and polished sections, partial chemical analyses, tests with the magnet, and *x*-ray powder photographs which were kindly made by Mr. S. V. Burr in the Department of Mineralogy. In this way the following iron-bearing minerals were identified: magnetite (Fe_3O_4), magnetic ferric oxide (γ-Fe_2O_3), goethite (α-FeO.OH), hematite (α-Fe_2O_3), siderite ($FeCO_3$), ankerite ($(Ca,Mg,Fe)CO_3$, and the hydrated microcrystalline to cryptocrystalline varieties of goethite and

[1]Work done in the Departments of Geology and Mineralogy, University of Toronto, with the aid of a fellowship of the National Research Council, and published with the permission of the Council.

hematite named limonite and turgite, respectively. Of these minerals only goethite (limonite) and hematite (turgite) were identified by their *x*-ray powder patterns; the remaining minerals mentioned were recognized in other ways.

FLOAT ORE AND DRILL CORE

The common type of float ore and drill core is a hard, brown, compact material consisting of goethite, limonite, hematite, turgite, and quartz in widely varying amount, giving an ore which ranges

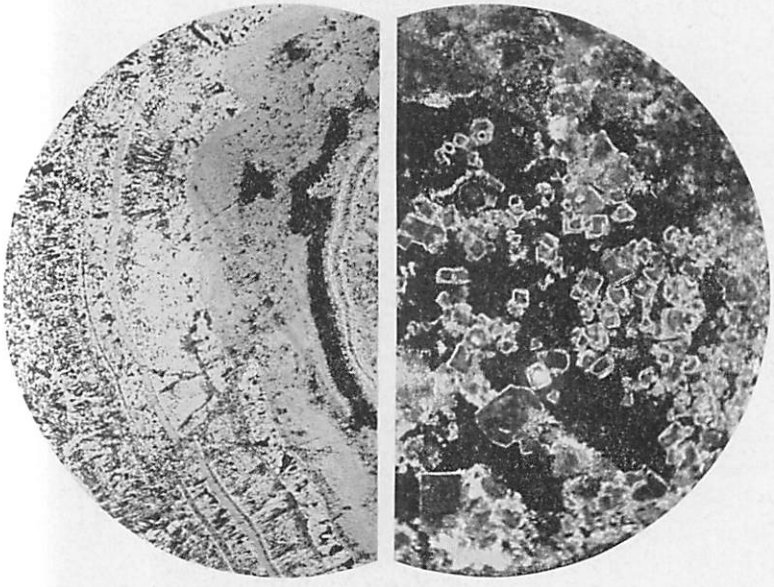

FIG. 1 (*left*).—Colloform turgite (lighter grey) and limonite (darker grey). Float ore from Wagita Bay. Reflected light (× 16).

FIG. 2 (*right*).—Turgite (black), goethite and limonite (light and dark grey), apparently pseudomorphus after pyrite. Float from Floatore Island. Transmitted light (× 41).

from nearly pure iron oxide to ferruginous chert. The streak of the massive ore varies from the ochre yellow of goethite to the dark red of hematite. Some of the specimens of float ore show small vugs whose walls are formed by convex surfaces indicating an internal

botryoidal structure. Such surfaces are occasionally encrusted with minute brilliant crystals of goethite[2] and quartz.

The internal botryoidal or colloform structure of a specimen of float ore appears in polished section (Fig. 1) which shows alternating shells of radial-fibrous turgite and limonite. Another type of float ore is illustrated in Fig. 2, which shows turgite with goethite and limonite, apparently pseudomorphous after pyrite.

TABLE 1

PARTIAL ANALYSES OF IRON ORES FROM THE VICINITY OF STEEPROCK LAKE

	1	2	3	4
SiO_2	....	1.10	2.42	2.08
Al_2O_3	....	0.29	1.44	2.51
Fe_2O_3	....	....	93.37	95.38
FeO	....	....	1.34	....
H_2O+	11.59	9.11	1.19	1.06
H_2O-		0.22		
P_2O_5	....	0.07	....	....
CO_2	....	....	0.83	....
			100.59	101.03

1. Limonite (goethite pattern), colloform, fibrous, from Rawn pits, S. of Falls Bay. 2. Goethite (goethite pattern), massive, fine grained, from Floatore Island. 3. Turgite (hematite pattern), concentric, fibrous, from Wagita Bay. 4. Hematite and turgite (hematite pattern), colloform, concentric, from Overflow.

The analytical results in Table 1, together with the *x*-ray evidence, indicate the appropriate names for the analysed materials. No. 1, with more than the theoretical H_2O-content of goethite, is named limonite. No. 2 is goethite. Nos. 3 and 4, with appreciable H_2O, are turgite or contain this hydrated variety of hematite.

TABLE 2

LOSS ON IGNITION OF SAMPLES OF DRILL CORE FROM STEEPROCK LAKE

No.	Loss	No.	Loss	No.	Loss	No.	Loss
15	0.22	7	1.28	3	3.22	8	4.78
13	0.48	16	2.38	12	3.24	17	6.54
2	0.76	9	2.68	18	3.46	1	7.81
10	1.25	5	2.76	6	3.52	14	8.85
						4	9.01

[2]A goniometric and *x*-ray study of these crystals was made by Professor M. A. Peacock (1942), assisted by Mr. E. W. Nuffield.

Table 2 gives the percentage loss on ignition, or roughly the H_2O-content, of seventeen samples of iron ore from the drill cores. With a streak ranging from red to yellow and with H_2O rising from 0.22 to 9.01, the samples appear to be essentially hematite with increasing admixture of goethite.

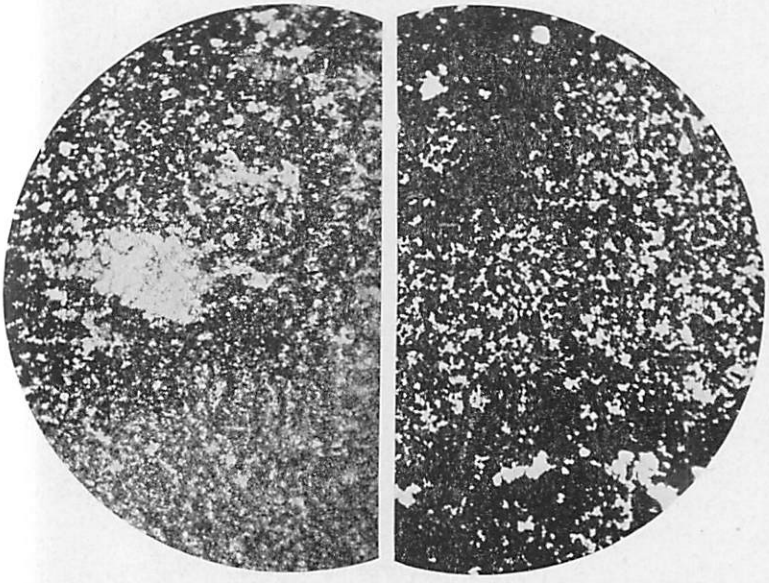

FIG. 3 (*left*).—Limonite (black), siderite (grey with high relief), quartz (white), and ankerite (large light grey crystals). Weathered siderite iron formation, E. side of East Arm. Transmitted light (× 41).

FIG. 4 (*right*).—Goethite and limonite (black) and quartz (white). Siliceous float ore from Floatore Island. Transmitted light (× 82).

CARBONATE AND MAGNETITE ROCK

The iron formation exposed along the East Arm of Steeprock Lake consists of banded siderite and chert altered in places by gabbro and diabase intrusions to banded magnetite and quartz. Siderite is superficially altered to limonite and magnetite is partly altered to magnetic ferric oxide, showing that both types have undergone some oxidation. Fig. 3 shows a thin section of the carbonate iron formation; Fig. 4 represents siliceous float ore.

MINERAL RELATIONS AND ORIGIN

The minerals observed in the iron ores of Steeprock Lake and the alterations noted in the iron minerals, namely limonite and goethite after pyrite (Fig. 2), limonite after siderite (Fig. 3), magnetic ferric oxide after magnetite, and limonite after magnetite, all point to deposition and alteration at low temperatures. The absence of veining in the hand specimens and in the thin sections speaks against the introduction of iron from an external source. The restriction of the lean iron formation to a definite horizon in the steeprock series, above a limestone series and below a series of lavas and pyroclastics, indicate that the iron ores originated as sediments.

Although the present observations are insufficient foundation for a detailed theory of origin, they suggest that the iron ore was concentrated by sedimentary agencies, forming a banded siderite chert, and that the present ore is due to enrichment by oxidation of the slightly metamorphosed ferruginous beds. The oxidation appears to have been due mainly to meteoric waters, but it may have been aided by brecciation and heat caused by the post-Steeprock gabbro intrusives.

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THE WALKER MINERALOGICAL CLUB

OFFICERS FOR 1941-1942

Honorary President.....Professor T. L. Walker
President.....Mr. W. E. Chantler
Secretary-Treasurer.....Dr. V. B. Meen
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1940-3.....Mr. J. G. Dickenson
1939-42.....Mr. G. E. Steel
Councillor for Department of Mineralogy.....Professor M. A. Peacock
Councillor for Student Members.....Mr. J. R. Charlton
Past President.....Professor Ellis Thomson
Editor.....Professor A. L. Parsons

FIRST MEETING

The first meeting of the season 1941-2 was held on October 23 at 8.00 P.M. in the home of Mr. George Steel, Councillor of the Club, at 37 Mason Boulevard, Toronto.

The President, Professor Ellis Thomson, occupied the chair. The Secretary read the report of the Nominating Committee which had recommended the following gentlemen:

President.....Mr. W. E. Chantler
Secretary-Treasurer.....Dr. V. B. Meen
Councillors for Ordinary Members
For 1940-3 (replacing Dr. W. S. Dyer, deceased).....Mr. J. G. Dickenson
1941-4.....Mr. W. C. Ringsleben
Councillor for Department of Mineralogy.....Professor M. A. Peacock
Councillor for Student Members.....Mr. J. R. Charlton

It was moved by Professor Parsons and seconded by Mr. Percy Hopkins that the report be accepted and that ballots for the election of officers be sent out; that the poll close December 11 and that the Council be instructed to canvass the ballot and announce the results at the December meeting.

The Editor, Professor Parsons, gave his report and announced the sending out of the *Contributions to Canadian Mineralogy* to each member in good standing.

Mr. Steel exhibited his fine collection of minerals and demonstrated to the members the cutting and polishing of minerals. Mr. Grant Waite demonstrated the polishing of gem stones on his polishing lap which he had kindly brought along. Mr. Chantler and Dr. Meen demonstrated the fluorescence and phosphorescence of some minerals.

At the close of the meeting refreshments were served by Mrs. Steel, kindly assisted by the wives of some of the members.

It was moved by Professor Parsons that the thanks of the Club be extended to Mr. and Mrs. Steel for the very enjoyable evening, and to Mr. Waite, Mr. Chantler, and Dr. Meen for their part in the programme.

SECOND MEETING

The second meeting was held on December 18 in Room 56 of the Mining Building, University of Toronto, at 5.00 P.M. The retiring President, Professor Ellis Thomson, occupied the chair. The Secretary read the results of the ballot for officers who were elected as nominated. The new President, Mr. W. E. Chantler, then took the chair. Professor Parsons proposed a vote of thanks for the outgoing officers.

Mr. W. B. Timm, Director, Mines and Geology Branch, Ottawa, gave a most interesting talk on the subject "War Minerals." The many minerals necessary in war time were mentioned and the sources and uses discussed. Mr. Timm's address was published in full in *The Northern Miner*.

A motion of thanks to Mr. Timm, proposed by Professor Parsons and seconded by Professor Thomson, was carried.

THIRD MEETING

The third meeting of the season was held in Room 56, Mining Building, University of Toronto, at 5.00 P.M. on February 19, 1942. In the unavoidable absence of the President, Mr. W. E. Chantler, because of war work, the Past President, Professor Ellis Thomson, occupied the chair. There was no official business.

The speaker of the afternoon was Professor H. V. Warren of the University of British Columbia, whose subject was "Recent Mineral Development in British Columbia." Professor Warren dealt with the work done by his department at the University in promoting the search for war minerals in British Colunbia, and the numerous economic successes of the last few years were pointed out.

An expression of thanks was tendered the speaker by Dr. E. M. Burwash. Questions were asked by Messrs. J. Dawson, P. Hopkins, L. G. Smith, and Professor Parsons.

FOURTH MEETING

The fourth meeting was held in Room 26 of the Mining Building, University of Toronto, at 8.00 P.M. on April 23, with Mr. W. E. Chantler, President, in the chair.

Professor Parsons moved that a nominating committee be appointed to nominate officers for the year 1942-3 and report their nominations at the October meeting. Professor Thomson seconded the motion.

Mr. E. W. Nuffield gave an account of joint work with Professor M. A. Peacock on the optical properties of goethite, describing the new effect of re-crossing of the optical axial plane with varying wavelength and temperature (pp. 53-61).

Mr. S. V. Burr described the results of a collaboration with Dr. Peacock on the hitherto unknown alloys of palladium and bismuth, among which four compounds were found in addition to the end-phases (pp. 19-31).

A motion of thanks to the speakers for their interesting addresses was proposed by Professor Thomson and unanimously approved.

The membership of the Club as on June 27, 1942, is as follows:

Honorary Members	3	
Ordinary Members	248	paid
Student Members	9	

There are 18 members known to be on active service. The Club has lost two members, Messrs. Joseph Errington and B. W. Hartley, by death during the year.

FINANCIAL STATEMENT OF THE WALKER MINERALOGICAL CLUB FROM JUNE 21, 1941, TO JUNE 22, 1942

June 21, 1941, Cash on hand and in bank		$242.21
RECEIPTS		
Dues	$268.50	
Sales of Journal	6.00	
Bank Interest	1.14	
Exchange less bank charges	4.33	
University of Manitoba, for half-tones in 1942 issue	50.00	
		$329.97
		$572.18
EXPENDITURES		
Oct. 18, 1941, Postage	$ 22.00	
Nov. 16, " Postage	4.00	
Nov. 25, " University of Toronto Press	21.88	
Dec. 10, " University of Toronto Press	6.38	
Jan. 21, 1942, Postage	2.50	
Feb. 10, " University of Toronto Press	6.16	
Feb. 27, " University of Toronto Press	284.21	
Mar. 25, " University of Toronto Press	5.67	
April 15, " Postage	5.00	
May 6, " University of Toronto Press	3.24	
		$360.64
June 22, 1942, Cash on hand and in bank		$211.54
		$572.18

V. B. MEEN,
Secretary-Treasurer

June 27, 1942.