

Marshite, Miersite and Iodyrite from Broken Hill, New South Wales.

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MINERALS containing iodine as an essential constituent are of rare occurrence in nature. The most common, and that first described, is silver iodide, which was analysed by Vauquelin in 1825; hexagonal crystals of iodyrite were described by Des Cloizeaux in 1854. Other iodides are marshite and the new mineral miersite; iodobromite and schwartzembergite also contain considerable amounts of iodine. The existence of mercury iodide seems to be doubtful; the supposed mercury iodide from Broken Hill consists of an intimate mixture of cinnabar and iodyrite.¹ Two iodates are also known, namely lautarite and dietzeite.

I. MARSHITE.

Crystals of "native copper iodide" were discovered at Broken Hill, New South Wales, by C. W. Marsh,² in 1892. The results of his qualitative analysis showed the presence of copper and iodine, and the crystallographic form was stated to be "tetragonal-hemihedral." In an abstract of this paper Prof. Miers³ pointed out with reference to the statement of the crystalline form: "hier ist wohl ein Fehler, denn Krystalle von derselben Substanz, die im britischen Museum sich befinden, sind tetraëdrisch und gehören dem regulären Systeme an."

It is possible that Marsh made his crystallographic observations on either wulfenite or stolzite, both of which minerals have several times

¹ Silver iodide is extracted when the substance is digested with a solution of potassium iodide. See also J. B. Jaquet, "Geology of the Broken Hill Lode and Barrier Ranges Mineral Field, New South Wales," *Memoirs Geol. Survey, N.S.W.*, 1894, Geol. Ser. No. 5, p. 90.

² *Journal and Proc. Roy. Soc. New South Wales*, for 1892 [1893], XXVI. 326 (Abstract *Min. Mag.* XI. 236). The principal characters of the mineral were verified by Prof. A. Liversidge, who in an accompanying note (p. 328) proposed the name marshite. A later brief description of the mineral is given by G. W. Card, *Records Geol. Survey, N.S.W.* 1895, IV, 131.

³ *Zeits. Kryst. Min.* 1894, XXIV. 207.

been sent to the British Museum labelled as marshite. The crystal of marshite measured by Prof. Miers was isotropic; it was bounded by faces of the cube and of two tetrahedra, and was twinned on a tetrahedron face.

Tetrahedral crystals of cuprous iodide have been prepared by E. Meusel¹ by the action of hydriodic acid on metallic copper or on copper-glance. Although a quantitative analysis has not been made of marshite, it is without doubt identical with this artificial cuprous iodide.

Occurrence; Physical Characters.—The description of the mineral to be now given is based on an examination of seven specimens in the British Museum collection, all of which are from Broken Hill. Labels with three of the specimens give the exact locality as the Broken Hill Proprietary Consols Mine.

The crystals of marshite are usually scattered over the surface of platy or cellular psilomelane, which in turn encrusts an incoherent mixture of limonite and cerussite² with grains of quartz and grains and dodecahedra of brown garnet. Sometimes copper-glance or cuprite is also present, the latter in good crystals altered on the surface to malachite. On one specimen the psilomelane forms a thin coating on blue opalescent quartz. The matrix of another specimen consists of massive and crystallised cuprite, with some native copper, quartz and brown garnet.

The faces of the crystals are bright and have a resinous to adamantine lustre. The colour varies from very faint yellow to dark brick-red, but the streak is always bright lemon-yellow. For an almost colourless crystal to give a bright yellow streak is very striking. Exposure to bright sunlight for several days does not affect the colour. Only the very pale coloured crystals are transparent, the others varying from translucent to almost opaque according to the depth of colour.

An important character not before noticed is the perfect dodecahedral cleavage, $d\{110\}$. The fracture is conchoidal, and the mineral is rather brittle; hardness $2\frac{1}{2}$ on Mohs' scale.

The crystals and cleavage flakes are as a rule optically isotropic, but sometimes a broken crystal shows uneven extinction, as if strained. The refractive index was approximately³ determined for light of different colours with a colourless transparent prism of which the refracting

¹ Ber. deutsch. chem. Ges. 1870, III. 123.

² The cerussite shows stellated groups with twin-plane $m(110)$. A measured crystal was twinned on $r(130)$, and agreed closely with Mügge's description of cerussite from Broken Hill (Neues Jahrb. Min. 1897, II, 78).

³ The images were somewhat scattered.

angle of $35^{\circ} 13\frac{1}{2}'$ (calculated $35^{\circ} 16'$) was formed by a tetrahedron face and a dodecahedral cleavage.

$$n_{(Li)} = 2.813, n_{(Na)} = 2.846, n_{(Tl)} = 2.885.$$

For the extreme visible ends of the spectrum of white light the refractive indices are approximately 2.25 and 2.7. The dispersion is thus considerably higher than in diamond.

Crystallographic Characters.—Two types of the marshite crystals are to be distinguished; they may occur separately or together on the same specimen. On one specimen the crystals of type *A* pass into a continuous crust of ash-grey marshite, on which the larger and darker coloured crystals of type *B* are deposited. The crystals of the two types therefore appear to belong to two different periods of growth.

Type A.—Bright crystals usually scattered singly over the matrix; they are of minute size, but on one specimen measure 1.5 mm. across. The colour is usually pale wine-yellow, but varies from almost colourless to brighter yellow. Faces of the cube and of both tetrahedra are prominently developed (compare Fig. 1, p. 46), and some of the crystals are cubo-octahedral in habit.

Type B.—Crystals of this type are larger and average 1–1.5 mm. across. They vary in colour from orange-red to brick-red. The habit is distinctly tetrahedral, owing to the small development or absence of one tetrahedron, and of the cube. The crystals are often grouped together in parallel position.

Although a dozen crystals (of both types) were measured on the goniometer, the only forms noticed were the cube $a\{100\}$ and the two tetrahedra $+o\{111\}$ and $-o\{1\bar{1}1\}$. The measurements were usually good, and agreed closely with the calculated angles of cubic crystals.

The faces of both tetrahedra are bright and smooth; they show no difference in character, and on some crystals of type *A* they are of equal size. The cube faces are slightly striated parallel to their intersection with either the larger or the smaller tetrahedron faces. On crystals of type *B* the faces of the large tetrahedron are often striated and stepped parallel to their intersections with the cube faces, the edges of the steps being usually bounded by narrow planes in twin position relative to the main crystal. Juxtaposed twins with a tetrahedron face as twin-plane are frequent, and angles of $15^{\circ}48'$ ($=oa$) were often measured. Some crystals are twinned on more than one tetrahedron face.

The characters described above are remarkably like those of zinc-blende, and the refractive index is also nearly the same; the crystallographic

characters—habit, twinning and cleavage—are identical, and in fact some of the crystals, especially those of type *A*, are very similar in appearance to the crystals of yellow zinc-blende from the white dolomite of the Binnenthal in Switzerland, the figures of which given by Sadebeck and vom Rath may very well be taken to represent marshite.

Chemical Characters: Behaviour when heated.—Qualitative chemical tests made on crystals from two specimens showed the presence of only copper and iodine. These crystals, and also those from other specimens with one exception, when placed in a drop of cold dilute nitric acid, are quickly blackened on the surface owing to the liberation of iodine, and they are not reduced by zinc and sulphuric acid. Crystals from one specimen (of which the matrix is blue opalescent quartz) were found to contain a small amount of silver; these crystals are not blackened in cold dilute nitric acid, and they are reduced by zinc and sulphuric acid; they thus behave with these reagents like miersite (p. 42) and not like pure marshite (CuI.)

When heated on a microscope slide, the crystals become dark red and decrepitate; on cooling they regain their original colour. At a higher temperature the pure crystals blacken and decompose without fusing; but those which contain silver sometimes fuse to a reddish liquid, which on cooling solidifies to an aggregate of isotropic grains.

II. MIERSITE.

A preliminary account of miersite, named in honour of Dr. Henry A. Miers, F.R.S., Professor of Mineralogy in the University of Oxford, was given in *Nature*¹ for April 14th, 1898. A more detailed account has been deferred in the hope that sufficient material would be available for a quantitative chemical analysis. Six specimens of the mineral have now been found for the British Museum collection, but it would not be advisable to collect material for analysis from more than one, since the amount of copper varies in the different specimens.

Occurrence: Physical Characters.—All the specimens are from Broken Hill, New South Wales. The associated minerals are cerussite, limonite, malachite, brown garnet, and quartz, with sometimes copper-glance and cuprite which have escaped alteration. The miersite occurs on the free surface of the specimens, usually as crystalline crusts or as aggregates of rather indistinct crystals. Distinctly developed crystals are less frequent

¹ "Miersite, a cubic modification of native silver iodide." By L. J. Spencer. *Nature*, 1898, LVII, 574. The minute crystals on one of the specimens there mentioned have since been shown to belong to type *b* of iodyrite (see p. 46 below).

than in marshite. The crystals are sometimes about 2 mm. across, but usually they are much smaller.

The colour of the crystals and of the streak is canary-yellow, and it is not affected by exposure for several days to bright sunlight. The crystals are translucent, and have a resinous to adamantine lustre. The mineral is somewhat brittle, and has a hardness of $2\frac{1}{2}$: a crystal when crushed breaks into angular fragments without any distortion of the faces, and by this miersite is at once distinguished from iodyrite. The fracture is conchoidal, and there are, as in marshite, perfect cleavages parallel to the faces of the rhombic-dodecahedron, $d\{110\}$. Small fragments and cleavage flakes are transparent and, as a rule, perfectly isotropic.

Crystallographic Characters.—The crystallographic characters of miersite are exactly similar to those of marshite and zinc-blende. The habit varies from tetrahedral with narrow cube planes (compare Fig. 1, p. 46) to cubo-octahedral. Usually both tetrahedra are present and of different sizes, but they show no difference in surface characters. The crystals are frequently twinned, and this twinning may be more than once repeated, and on more than one tetrahedron face: as a result of this the angle $\alpha\alpha = 15^\circ 48'$ is of frequent occurrence. The faces are bright and smooth; those of the cube are sometimes striated parallel to the intersection with either the larger or the smaller tetrahedral faces. Tetrahedral faces show triangular striations and elevations, the edges of which are usually bounded by narrow planes in twin position relative to the main crystal. Although detailed measurements were made of more than a dozen crystals, these were the only forms noted. As a rule the measured angles only differed by a few minutes from the calculated cubic angles.

The habit of one of the measured crystals is that of a hemimorphic rhombohedral crystal of iodyrite with the forms $g\{55\bar{4}\}$ and $c\{111\}$. The planes prominently developed are three cube faces ($\bar{1}00$, $0\bar{1}0$, $00\bar{1}$), and one tetrahedron face (111), which is also the plane of twinning. On this crystal the perfect dodecahedral cleavage was purposely developed in five directions, and the cleavage flakes detached were perfectly isotropic. No pyroelectricity was detected on this, or any other crystal, by dusting a cooling crystal with red-lead and sulphur.

Chemical Characters: Behaviour when heated.—Qualitative chemical tests showed the presence of much silver and iodine, with varying amounts of copper. A very little chlorine may also be possibly present in some crystals. The mineral is not affected by dilute nitric acid, but is readily reduced by zinc and sulphuric acid. It is still hoped that sufficient material may be collected for a quantitative analysis.

The optical behaviour of the material after fusion, as described below, gives an approximate idea of the relative proportions of silver iodide and copper iodide. In these experiments only small amounts of material need be used, and comparative experiments can be made on mixtures of artificially prepared silver iodide and copper iodide in known proportions.

Fragments when heated on a microscope slide exhibit a more or less gradual change in colour, passing through bright orange-yellow to brick-red. There is no change in the transparency and isotropic character of the crystals either when hot or when cold. When heated to a higher temperature the crystals fuse to a deep-red liquid which spreads out as a film under the cover-glass. On solidification the substance is reddish-yellow and optically isotropic, and appears to be perfectly homogeneous. As further cooling takes place the colour gradually changes to bright-yellow, when all at once isotropic pale yellow needles commence to grow and branch out at numerous isolated points all over the field of view. These grow rapidly at the expense of the bright yellow substance, until the whole field is occupied by an intergrowth of two isotropic substances with sharp lines of demarcation between them. A little later the remaining bright yellow substance suddenly changes to very pale yellow birefringent iodyrite. This second change in state is the same as that which takes place with pure silver iodide (p. 49), and the sharp line separating the two modifications may be seen to sweep across the field of view from one side to the other; it does not, as in the first change of state, start independently from numerous isolated points.

The slide now, and when cooled to the ordinary temperature, shows an intergrowth of two substances: one isotropic and pale yellow, the other birefringent and paler in colour. The first usually forms a network of rods at angles of 70° – 75° or sometimes of nearly 90° , the interspaces of which are occupied by strips of the birefringent material; the latter extinguish parallel to their length and are opposed to quartz in the same direction. The relative amounts of these two substances varies considerably for different crystals; usually there is little or none of the birefringent iodyrite, while for crystals to be described later (p. 44) the isotropic substance is subordinate.

When weighed amounts of precipitated silver iodide and copper iodide in various molecular proportions¹ from $\text{AgI} + \text{CuI}$ to $8\text{AgI} + \text{CuI}$ were

¹ G. F. Rodwell has determined the sp. gr., melting points and coefficients of expansion and contraction of such mixtures, Proc. Roy. Soc. 1881, XXXIII, 143; Phil. Trans. 1883 (1882), CLXXIII, 1154, Plate 96; and M. Bellati and R. Romanese, from their determinations of specific heat and heat of transformation, conclude that molecular compounds are formed by silver iodide and copper iodide. Proc. Roy. Soc. 1882, XXXIV, 104; Phil. Trans. 1883 (1882), CLXXIII, 1169.

intimately mixed and fused on a microscope slide, the same phenomena were observed as with the natural crystals. The mixture $4\text{AgI} + \text{CuI}$ gave a slide showing the isotropic network with only a speck here and there of birefringent iodyrite. When more copper iodide was present the whole slide remained isotropic, while with more silver iodide more of the birefringent substance was formed.

The growth of the pale yellow isotropic crystals in the bright yellow isotropic substance is perhaps scarcely a simple change in state from an amorphous (or possibly cubic) modification to a cubic modification, since the crystals appear to have a definite composition (probably $4\text{AgI} \cdot \text{CuI}$), and the residue left after their growth consists of pure silver iodide. If this be the case, then during crystallisation there must be a migration of silver iodide through the solid material. It is, however, of course possible, that on the solidification of the material, two cubic substances, $4\text{AgI} \cdot \text{CuI}$ and AgI , are formed, and that each of these undergoes independently a change in state as the temperature falls first to one and then to another definite point.

Intergrowth with Iodyrite.—Crystals from two of the specimens differ considerably from those described above. They have the hardness and cleavage of miersite, but are paler in colour, and are doubly refracting. As a rule they are repeatedly twinned on two faces of the tetrahedron, and the prominent zone containing these two bright tetrahedral faces is deeply furrowed and striated. When viewed in polarised light across this striated zone, the crystals extinguish parallel to the zone-axis, and are opposed to quartz in the same direction. Cleavage flakes perpendicular to this zone-axis are seen, when viewed in parallel polarised light, to consist of three portions, which extinguish at angles of 60° to each other; each portion shows a very finely striated appearance (suggesting the intergrowth of two substances), extinction taking place parallel to the striations. Only rarely could portions of a positive uniaxial figure be distinguished. The refractive index was determined with a prism (bounded by a and d cleavage) from one of these crystals to be about $2\frac{1}{4}$ for the yellow part of the spectrum. Qualitative chemical tests showed the presence of silver and iodine with only a very small amount of copper; and fragments fused on a microscope slide show only a few of the isotropic bars. These crystals, therefore, appear to consist of an intimate and regular intergrowth of miersite and iodyrite. The nature of this intergrowth is suggested by the iodyrite crystals of type (b) (Fig. 1) described below.

Summarising the above observations, miersite may be defined as an optically isotropic, tetrahedral-cubic mineral, of which the composition is

probably $4\text{AgI}\cdot\text{CuI}$, and which mixes isomorphously with marshite (CuI) on the one hand, and on the other forms intimate intergrowths with iodyrite.

Possible identities.—When isomorphously mixed with a certain amount of marshite, the composition would become identical with that of “cuproiodargyrite” ($\text{AgI}\cdot\text{CuI}$). This mineral, from Iquique in Chili, is stated¹ to be brighter in colour and lustre, and to be harder and less sectile than iodyrite; the fracture is given as sub-conchoidal to splintery. These characters, so far as they go, agree better with those of miersite than with those of iodyrite, and it seems probable that “cuproiodargyrite” is intermediate between miersite and marshite, and not, as the name² suggests, a cupriferous variety of iodyrite.

Another mineral which may be mentioned here is the silver iodide from Chili, examined by Lawrence Smith.³ His two analyses of “an exceedingly pure specimen” showed the presence of traces of copper and chlorine; and he states: “One specimen that I saw had crystalline faces, indicative of the rhombic dodecahedron.” It is therefore possible that the material he examined may have been iodyrite intergrown with miersite. The silver iodide described by Domeyko⁴ also seemed to differ from iodyrite in being brittle and in sometimes giving “cleavage fragments with rhombohedral forms.”

III. IODYRITE.

Occurrence: Physical Characters.—The occurrence of iodyrite at Broken Hill is well known, but as yet no crystallographic description has been given. The several specimens from this locality in the British Museum collection show two distinct modes of occurrence:

(1) Pale sulphur-yellow crystallised material on a free surface often consisting of limonite or psilomelane; associated minerals are brown garnets, blue opalescent quartz, malachite, cerussite, cuprite, pyromorphite, anglesite, calamine (ZnCO_3), chessylite, or wad.

(2) Films or thin layers, of a rather brighter colour, on the surfaces of slickensides in white kaolin. They often show green stains, but the pure material free from these stains contains no copper.

¹ H. Schulze, *Chemiker-Zeitung*, 1892, XVI, 1952.

² Names of a similar construction are, however, frequently admitted into mineralogical nomenclature as species rather than as variety names, e.g. barytocalcite, cuprobismutite, galenobismutite, arsenopyrite, etc.

³ *Amer. Journ. Sci.* 1854 [ii.] XVIII, p. 374; U. S. Naval Astronomical Expedition to the Southern Hemisphere (1849-52), Vol. II, 1855, p. 96.

⁴ *Annales des Mines*, 1844, [iv], VI, p. 158.

The mineral is very soft (H about 1, or perhaps less) and sectile, so much so that the crystals can scarcely be touched without suffering distortion. The fracture is conchoidal, and the perfect basal cleavage shows a pearly lustre. Sometimes in freshly opened cavities the crystals are perfectly colourless and transparent with an adamantine lustre; they then somewhat resemble crystals of anglesite in appearance. On exposure to light the colourless crystals very soon assume the usual pale sulphur-yellow colour of iodyrite, and this is not further altered by prolonged exposure to bright sunlight. The streak is rather brighter yellow in colour with a tinge of green; it is shining and easily flakes off the paper.

Optically the mineral is uniaxial, with low positive double refraction. The tabular crystals and cleavage flakes, being so easily bent, usually show undulose extinction in parallel light, and in convergent light the optic figure is often distorted, sometimes resembling a biaxial figure; as a cleavage flake is moved about on the microscope stage the interference figure continually varies. Attempts to produce corrosion and percussion figures on the cleavage flakes were unsuccessful, and on none of the crystals could any pyroelectrical effects be detected.

The physical characters of iodyrite are considerably modified by the presence of a small amount of copper iodide: as explained above (p. 44) this copper may be assumed to be present as $4\text{AgI}\cdot\text{CuI}$ (miersite) occurring as an intimate intergrowth with the iodyrite.

Crystallographic characters.—Several crystals were measured on the goniometer, but no reliable determinations of the angles could be made, as few faces are developed, and the crystals are so easily distorted. The crystals are of two distinct types:

(a) Hexagonal plates or short prisms, with the forms $c\{111\}$, $m\{2\bar{1}\bar{1}\}$, and sometimes a narrow hexagonal pyramid near the position of $i\{5\bar{1}\bar{1}, \bar{1}11\} = 2P$, if placed as a pyramid of the first order. The prism and pyramid faces are usually striated horizontally. On one specimen the prisms are $1\frac{1}{2}$ cms. in diameter. On none of these crystals was a hemimorphic development observed.

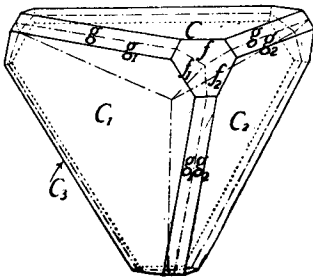


FIG. 1.

(b) Pseudo-cubic crystals, of tetrahedral habit, consisting of four simple rhombohedral crystals twinned together. Fig. 1 shows a compound crystal, and Fig. 2 the uppermost of the four simple crystals drawn in parallel position. These crystals cannot be distinguished by goni-

metric measurement from marshite and miersite: they are in fact mimetic crystals of iodyrite with the same external form as miersite and marshite.

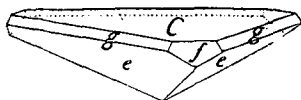


FIG. 2.

The twin-plane $e\{10.1.1\}^1 = \frac{3}{4}R$, is the same as that given by vom Rath² in his description of iodyrite crystals from New Mexico. He mentioned that three individuals were often arranged around a central one, but in these crystals, since the predominating form was $i\{\bar{1}11\} = -2R$, the twinning was rendered evident by the presence of re-entrant angles. In the crystals now described, $c\{111\}$ predominates in the compound crystal and corresponds to the regular tetrahedron. The smaller faces of $g\{55\bar{4}\} = -\frac{3}{2}R$ and $f\{7\bar{2}2\} = 3R$ correspond to the faces of the cube and the second tetrahedron respectively, two faces of g and three of f coming together. These compound crystals therefore show no re-entrant angles.

The angles measured on these pseudo-cubic crystals were not really good, but they agreed closely with the angles of cubic crystals. It is to be noted that the angles determined by von Zepharovich on artificial crystals of iodyrite vary slightly in one direction from cubic angles, while the measurements of Des Cloizeaux and of Seligmann³ on natural crystals vary slightly on the other side of cubic angles; this is shown in the table below:

	Seligmann.	Cubic angles.	Zepharovich.
$c : e\{10.1.1\} = \frac{3}{4}R$	35°14'	$od = 35°16'$	35°22'
$c : g\{55\bar{4}\} = -\frac{3}{2}R$	54°42'	$oa = 54°44'$	54°50'
$c : f\{7\bar{2}2\} = 3R$	70°30½'	$oo = 70°32'$	70°36'
$c : c_1$	109°32'	$oo = 109°28'$	109°16'
$g : g_1$	Salient 8'	0°	Re-entrant 24'

The compound nature of the crystals is very well shown by the examination in polarised light of cleavage flakes taken parallel to the faces of the pseudo-tetrahedron. In parallel light these show a dark equilateral triangle surrounded by narrow areas extinguishing parallel to the sides of the triangle and opposed to quartz in the same direction. In convergent

¹ The indices are much simplified if g be taken as $(100) = R$; the twin-plane then becomes (110) .

² F. A. Genth and G. vom Rath, Zeits. Kryst. Min., 1885, X, 473.

³ Zeits. Kryst. Min. 1882, VI, 229.

light the triangular portion shows in the centre of the field the usual positive uniaxial figure of iodyrite, while the borders show uniaxial brushes belonging to an axis outside the field of view. Usually, however, this structure is polysynthetic, and the same fragment may show, in parallel polarised light, several dark triangular areas and numerous lamellæ in three sets, each set of which extinguish together throughout the whole fragment.

These compound crystals of iodyrite are further twinned on a face, or sometimes on two faces, of the pseudo-tetrahedron, exactly like the crystals of marshite and miersite. As a consequence of this, re-entrant angles of about $15^{\circ}48'$ ($=\alpha\alpha$)¹ are frequent, and the narrow faces corresponding to the cube are deeply furrowed and striated. On account of this deep striation it was not possible to determine whether the very small angle ψ_1 (Fig. 1) is re-entrant or salient, and thus to decide whether the angles of Zepharovich or of Seligmann come nearer the truth.²

The pseudo-cubic crystals of iodyrite of type (*b*) differ essentially from the pseudo-cubic crystals of stannite described in this number of the Magazine (p. 56); these also are twinned on a pseudo-tetrahedron face. The iodyrite crystals were originally true cubic crystals, but are now paramorphs of iodyrite after the tetrahedral-cubic modification of silver iodide. Here the twinning is the result of the pseudo-cubic symmetry, whereas in stannite the twinning is clearly the cause of the pseudo-cubic symmetry. The case of iodyrite is similar to that of many cubic minerals showing optical anomalies which disappear at a higher temperature, *e.g.* boracite, leucite, cristobalite, etc. In the case of iodyrite, however, the two kinds of crystals are known to occur independently. The iodyrite crystals of type (*a*) must have been formed at a temperature below 146° (assuming atmospheric pressure), while those of type (*b*) were formed above this temperature. It may be noted that the structure of the compound crystals of iodyrite (Fig. 1, p. 46) is identical with that of crystals of eulytite described by Bertrand,³ and more fully, with figures, by Professor Lewis.⁴

¹ If *f* and *g* are present in the same zone $[2\bar{1}\bar{1}, 111]$ or $\{10\bar{1}, 111\}$ the angle $fg_1 = 16^{\circ}10'$ or $15^{\circ}30\frac{1}{2}'$, according as the angles of Zepharovich or of Seligmann are taken.

² A consideration of the fact that the *c* axis of iodyrite contracts with rise of temperature before the passage into the cubic modification takes place, suggests that Zepharovich's angles are the more accurate, since with increase in temperature they will gradually approach those of cubic crystals.

³ Bull. Soc. Min. de France, 1881, IV, 61: compare, however, R. Brauns, Die optischen Anomalien der Krystalle, 1891, p. 333.

⁴ Treatise on Crystallography, Cambridge, 1899, p. 478.

Behaviour when heated.—The change in state which silver iodide undergoes at a temperature of about 146° C. is well known. Talbot (1838)¹ first observed that when a film of silver iodide is warmed, its colour changes from pale sulphur-yellow to bright yellow; and various observers² have since shown that the pale yellow variety, which exists at ordinary temperatures, is birefringent and hexagonal, and that with an increase of temperature these crystals undergo a contraction in the direction of the hexagonal axis and an expansion in the directions perpendicular to this axis, while the total volume of the crystal diminishes. When the temperature reaches about 146° C., there is a further sudden contraction of considerable amount accompanied by a change in colour, thermal capacity, electrical conductivity and optical refraction—a denser, cubic and isotropic modification of silver iodide being then called into existence. The same change also takes place at the ordinary temperature, under a pressure of about 3000 kilos per sq. cm. These changes are reversible: on diminution of temperature or pressure the pale yellow hexagonal modification again appears.

When a cleavage plate of iodyrite is heated on a microscope slide there is, at a definite temperature, a sudden change from the pale yellow colour to a bright orange yellow, and at the same time the plate becomes optically isotropic. On cooling, the pale yellow colour suddenly reappears, and the plate is seen, between crossed nicols in parallel light, to become birefringent. The plate, after being heated above this critical temperature, is cloudy, and no longer shows the perfect cleavage nor the uniaxial optic figure, since it now consists of an aggregate of differently orientated crystals of iodyrite.

At a still higher temperature the colour becomes brick-red, and the substance fuses to a deep-red liquid which is almost black by reflected light and which spreads out as a film under the cover-glass. On cooling again, the mass remains isotropic, while the colour gradually changes from brick-red to bright yellow; then follows a sudden change to the pale yellow birefringent modification, and the line of demarcation between the two can be seen to sweep quickly across the field of view. The slide then shows an aggregate of interlocking lath-shaped crystals, often of considerable size and showing brilliant polarisation colours. The longer direction

¹ H. F. Talbot, *Phil. Mag.* 1838, XII, 258.

² Fizeau (1867), Wernicke (1871), Rodwell (1874, 1876), Lehmann (1877), Bellati and Romanese (1882), Kohlrausch (1882), Mallard and Le Chatelier (1883-5), Schwarz (1892).

of the laths is perpendicular to the principal axis of the iodyrite crystals. With the aid of a micro-spectroscope the change in state on cooling is seen to be accompanied by a sudden increase in the length of the blue end of the spectrum.

IV. MUTUAL AND OTHER RELATIONS.

As explained above, marshite and tetrahedral-cubic silver iodide are isomorphous. The latter when pure is only stable at a temperature higher than 146° , but when it contains a certain amount of copper (5.6 per cent. would be required by the formula $4\text{AgI}.\text{CuI}$) it is stable at ordinary temperatures, and is then distinctive enough to receive the special name miersite. Larger amounts of copper may be present as an isomorphous mixture of marshite; while any excess of silver iodide will, at the ordinary temperature, be represented as iodyrite intimately intergrown with the miersite.

Silver iodide appears to exist also in a third form and therefore to be trimorphous. This is holohedral-cubic and isomorphous with members of the cerargyrite group. It is represented by the AgI in iodobromite ($2\text{AgCl}.\text{2AgBr}.\text{AgI}$), and as smaller amounts in cerargyrite, embolite and bromargyrite. It may here be mentioned that a mineral¹ similar to *iodobromite* occurs at Broken Hill in New South Wales and at Chañarillo in Chili. At both these localities it is usually associated with iodyrite, and consists of cubo-octahedra of a bright orange-yellow colour, which soon alters to dark green on exposure to light. The crystals are translucent, and are so tough and sectile that fragments cannot be detached for optical examination without distortion: $H = 2\frac{1}{2}$. There is no distinct cleavage. Chemical tests showed the presence of silver, iodine, bromine and chlorine, all in considerable amount.

The characters of the three modifications may be compared in the following table:

	Iodyrite.	Miersite.	Iodobromite.
System	Rhombohedral	Cubic	Cubic
Class	Hemimorphic	Tetrahedral	Holohedral
Twin-plane	A Rhombohedral face	A tetrahedral face	Not twinned
Cleavage	Perfect basal	Perfect dodecahedral	Indistinct octahedral?
Optically	Uniaxial	Isotropic	Optically anomalous?
	$cg = 54^{\circ}42'$ or $54^{\circ}50'$	$oa = 54^{\circ}44'$	$oa = 54^{\circ}44'$

¹ An analysis and detailed description of this will be published later. The mineral from Chili was long ago described as cubic silver iodide, by A. Dufrénoy, *Traité de Minéralogie*, 2nd Edit., 1856, Vol. III, pp. 452, 460.

Really, however, these three modifications of silver iodide only exist as minerals in isomorphous mixtures influenced by the mass effect of other substances, or in definite molecular compounds. They may or may not be identical with the three modifications mentioned by G. F. Rodwell.¹

The possible existence of two cubic modifications of a compound containing silver iodide has also been suggested above (p. 44) from the behaviour of mixtures of silver iodide and copper iodide when heated. They are also possibly related to the two cubic modifications of mixed crystals of ammonium chloride, bromide and iodide produced by O. Lehmann²; these are, however, not beyond doubt, as pointed out by Arzruni.³

Lehmann⁴ has stated that the cubic modification of silver iodide which is stable above 146° crystallises in octahedra and is isomorphous with cerargyrite: from the present observations, however, it would seem to be the tetrahedral-cubic modification isomorphous with marshite which crystallises out above this temperature.

As mentioned above (p. 47) there is a close connection between the angles of iodyrite and the angles of a cubic crystal; and between miersite and iodyrite there is a still further similarity in the development of the crystals. Some crystals of miersite have the habit of hemimorphic-rhombohedral crystals of iodyrite, while in iodyrite of type (*b*) the habit is identical with that of miersite. These close relations indicate that there must be similarity in crystalline structure,⁵ as is often the case with dimorphous minerals, for example, zinc-blende and wurtzite, orthoclase and microcline. In such cases Mallard⁶ has suggested the essential identity of these pairs of minerals, the one of higher symmetry being the result of ultra-microscopic twinning of the one of lower symmetry. In the same way crystals of iodyrite of type (*b*) might by repeated twinning give rise to isotropic crystals identical with miersite; but here, as in the case of zinc-blende, the perfect rhombic-dodecahedral cleavage would be difficult to explain, unless it were a parting parallel to the twin-planes ϵ of iodyrite, which, in the compound crystals, coincide in direction with the faces of the rhombic-dodecahedron.

¹ Proc. Roy. Soc. 1874, XXIII, 108; Phil. Trans. 1883 (1882), CLXXIII, 1134.

² Zeits. Kryst. Min. 1885, X, 321; "Molekularphysik," 1888, I, 792.

³ Physik. Chemie d. Krystalle, 1893, p. 321.

⁴ Zeits. Kryst. Min. 1877, I, 492; "Molekularphysik," 1888, I, 166.

⁵ Related kinds of groupings of the atoms of silver iodide in the rhombohedral and cubic modifications have been suggested by Prof. W. J. Sollas, Proc. Roy. Soc. 1898, LXIII, 289.

⁶ Bull. Soc. Min. de France, 1882, V, 325; Ann. des Mines, 1876, [vii], X, 157.

When crystals of iodyrite were first described by Des Cloizeaux, he noticed that in the angles there was a very close relation to greenockite. This relation may also be extended to other mineral species, as shown in the following table :

			$a : c$	Cleavage.
Iodyrite.....	AgI	} Hemimorphic- } rhombohedral. } Optically+	1 : 0·8196	c perfect
Wurtzite .. .	ZnS		1 : 0·8175	a c
Greenockite	CdS		1 : 0·8109	a c
Zincite	ZnO		1 : 0·8109	c perfect

These minerals are placed by F. Rinne¹ in the "magnesium type" of his isotypes: other members are magnesium ($c=0\cdot8195$), niccolite ($c=0\cdot8194$), ice ($c=0\cdot8085$), tridymite ($c=0\cdot8265$), lead iodide ($c=0\cdot8379$), and many others, all of which are chemically simple substances. Some of these are dimorphous, and form another parallel series :

Miersite	(Ag,Cu) I	} Tetrahedral-cubic. } Twinned on a tetrahedron face. } Perfect dodecahedral cleavage.
Zinc-blende	Zn S	
Marshite.....	Cu I	

Nantokite² (CuCl) probably belongs to this series. Numerous other substances crystallise in both cubic and rhombohedral modifications (*e.g.* carbon as diamond and graphite), but they do not appear to belong to these series.

Now it will be seen from the above tables that the same relation exists between iodyrite and miersite as exists between wurtzite and zinc-blende :

Hemimorphic- rhombohedral.	Tetrahedral- cubic.	Holohehdral- cubic.
Iodyrite Wurtzite	Miersite Zinc-blende	Iodobromite (Schalenblende) ?

As far as crystallographic characters are concerned this is a perfect example of an isodimorphous (perhaps isotrimorphous) group, but

¹ Neues Jahrb. Min. 1894, I, 1; 1897, II, 1; Zeits. physik. Chemie, 1895, XVI, 529.

² The cubic cleavage given by Breithaupt requires verification.

apparently the only chemical relation existing between zinc sulphide and silver iodide is that their simplest conceivable molecules contain two atoms. Isomorphous replacement¹ does not occur, and no apparent relation is shown by the molecular volumes. Isomorphous replacement, however, takes place between miersite and marshite, and between iodobromite and cerargyrite; in the former between the metals, and in the latter between the haloids.

¹ Mentzel has found iodine in a cadmiferous zinc ore from Silesia. *Ann. des Mines*, 1829 [ii], V, 324; *cf.* Dana, *System of Mineralogy*, 6th Edit. 1892, p. 161.
