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On the structure of Perovskite from the Burgumer Alp, Pfitschthal, Tyrol.

By H. L. BOWMAN, M.A.
Demonstrator of Mineralogy in the University of Oxford.

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I. INTRODUCTORY AND HISTORICAL.

THE question of the system to which perovskite should be referred, and the explanation of the discrepancy between its form and optical properties, have been the subject of much discussion among crystallographers ever since the discovery by Des Cloizeaux, in 1858, of the double refraction of crystals of calcium titanate from Zermatt, having the same composition as the crystals of cubic form from the Ural Mountains, to which the name perovskite had been given by G. Rose in 1839.

It is unnecessary here to give in detail the earlier history of the controversy, as a full account of this has already been published in monographs by A. Ben Saude [1] and P. J. Holmquist,[2] but it will be necessary to refer in some detail to the later work by Baumhauer,[3] Ben Saude, and other writers.

The material previously investigated has been derived principally from four sources:—the Ural Mountains, Zermatt, the Pfitschthal in Tyrol, and Arkansas. The crystals are all of cubic habit, with the

[1] A. Ben Saude, 'Über den Perowskit.' Preisschrift, Göttingen (Dieterich'sche Buchdruckerei), 1882. Reviewed by Tschermak (Min. Petr. Mitt., 1882, vol. v, p. 194); by Baumhauer (Zeits. Kryst. Min., 1883, vol. vii, p. 612); and by Klein (Neues Jahrb. Min., 1884, vol. i, p. 175).

[2] P. J. Holmquist, 'Synthetische Studien über die Perowskit- und Pyrochlormineralien.' Inaug.-Diss., Upsala, 1897; Bull. Geol. Inst. Univ. Upsala, 1897, vol. iii, pp. 181–268.

[3] H. Baumhauer, Zeits. Kryst. Min., 1880, vol. iv, p. 187.

exception of those from Arkansas, which are octahedral. These latter are, however, perhaps not true perovskite, as they have been found by Mar [1] to contain niobium and tantalum, and to be intermediate between perovskite and dysanalyte.

There is a general agreement among observers that, geometrically, the crystals of perovskite are referable to the cubic system; a number of forms having been described, whose faces, though in many cases not holohedrally developed, are yet similarly distributed about the three axes, in accordance with cubic symmetry.

The optical properties have been examined in detail, more particularly by Des Cloizeaux [2] and Ben Saude [3], who agree in finding the crystals strongly birefringent and biaxial. All the crystals, with the exception of those from Tyrol (see p. 159), are described as having in places a more or less regular lamellated structure parallel to the faces of the cube, with extinction parallel to the diagonals of the cube-faces, and showing in convergent polarized light hyperbolic brushes, like those observable in plates perpendicular to a third mean line. In other places there are diagonal lamellae showing a single, normally-emergent (biaxial) optic axis.

The method of etching was first applied to these crystals by Baumhauer,[4] and the etching figures were studied in connexion with the optical properties by himself and by Ben Saude. These observers obtained on the cube-faces, by means of hydrofluoric acid, two distinct types of etching pits in different parts, viz:—

(*a*) rhombic pits, which lie in symmetrical positions on adjacent lamellae parallel to cube-faces;

(*b*) linear or elongated pits, lying parallel to cube-edges and in two mutually rectangular positions on adjacent diagonal lamellae.

The shapes of the linear pits described by the two authors are somewhat different, probably owing to the use by the former of reflected light, a method which (as pointed out by Ben Saude) is wanting in precision. The orientation of the rhombic pits is also differently stated by them, those observed by Baumhauer being symmetrical to

[1] F. W. Mar, Amer. Journ. Sci., 1890, vol. xl, p. 403. See also C. Hintze, 'Handbuch der Mineralogie'. 1897, vol. ii, p. 1651.

[2] A. Des Cloizeaux, Ann. d. Mines, 1858, sér. 5, vol. xiv, p. 417; Nouvelles Recherches, 1867, p. 84; Mém. de l'Acad. Francaise, 1868, vol. xviii, p. 594; Neues Jahrb. Min., 1875, p. 279, 1877, pp. 160 and 503, 1878, p. 43; Bull. Soc. franç. Min., 1893, vol. xvi, p. 218.

[3] A. Ben Saude, loc. cit., p. 15.

[4] H. Baumhauer, loc. cit.

the cube-diagonals,[1] while those described by Ben Saude had one of their edges parallel to an edge of the cube.

The areas showing these two types of pits coincide with those defined by the optical characters. Ben Saude found, however, by using high magnification, that the lamellae with rhombic pits are themselves composed of narrower lamellae, which show different colours and sometimes slight differences of extinction, and that the pits extend across these without disturbance.

Treatment with fused caustic potash, on the other hand, gave rise to square pits with edges parallel to the diagonals of the cube-face, in place of the rhombic pits produced by hydrofluoric acid.

Etching figures on faces of the dodecahedron or octahedron were not obtained by these observers; but sections parallel to the dodecahedron, examined by Ben Saude, showed in polarized light three kinds of areas, viz.:—

(1) areas extinguishing parallel to the intersections of the face with the cube, and showing a normally-emergent bisectrix;

(2) (3) Two sets of bands lying at about 58° to the cube-edge in either direction, and extinguishing at 45° to that edge.

The observations of Baumhauer and Ben Saude were thus in most respects in agreement, but the explanations of the structure proposed by them were widely opposed.

Baumhauer, adopting the view proposed by Des Cloizeaux,[2] considered the crystals to be mimetic and to consist of orthorhombic material, the (pseudo)-cube being in reality a combination of an orthorhombic prism $\{110\}$ and the basal pinacoid $\{001\}$, with a prism-angle of 90° (corresponding to the axial ratios, $a:b:c = 1:1:0{\cdot}7071$), and the lamellation being due to twinning on the faces of $\{111\}$. He also described the existence of twinning on faces of $\{110\}$. The rhombic etching pits would then be characteristic of $\{001\}$,[3] while the linear pits would indicate the prism-faces. The optic axial plane would be parallel to (001), and the axial angle $2V = 90°$, so that one optic axis emerges perpendicular to each prism-face.

[1] H. Baumhauer, Zeits. Kryst. Min., 1880, vol. iv, pp. 189, 197; and 1883, vol. vii, p. 612.

[2] A. Des Cloizeaux, Neues Jahrb. Min., 1878, p. 43.

[3] Ben Saude laid stress on the orientation of these pits, as observed by himself and (as he supposed) also by Baumhauer, not being in accord with the symmetry of the basal pinacoid of an orthorhombic crystal. Baumhauer, however, explained later (Zeits. Kryst. Min., vol. vii, p. 612) that the pits observed by him were as above described, and had been wrongly drawn in Zeits. Kryst. Min., vol. iv, plate 7, figs. 1 and 3.

Tschermak also considered perovskite to be mimetic, and in a review of Ben Saude's work[1] drew from his observations the conclusion that it belonged to the monoclinic system, and that the (pseudo)-cube was composed of the forms {100}, {001}, and {010}, the first two having linear, and the last rhombic pits; with lamellated twinning on (100), (010), and the prism-faces. This removal of perovskite to the monoclinic system was suggested in order to account for the orientation of the rhombic pits described by Ben Saude.

Ben Saude, on the other hand, rejected Baumhauer's view, chiefly owing to his observation that where the lamellae are crossed by a crack they frequently show a sudden change in breadth and in their polarization-colours[2]—a character which he held to be incompatible with their being crystalline individuals in twin position, and to mark them as of secondary origin, and as not belonging to the substance in its original condition. He considered the etching figures to be untrustworthy as evidence of the symmetry of the crystal, on account of the (supposed) difference in the symmetry of the pits produced by different solvents, and of the extension of the pits across the optical boundaries. He concluded that perovskite was in fact cubic (pyritohedral), and that the double refraction was produced 'durch Änderung der ursprünglichen Gleichgewichtslagen beim Wachsthum der Krystalle'.

As pointed out by Mallard,[3] this conclusion hardly seems to follow from the observations described, which rather indicate that 'all crystals of perovskite, from whatever locality, possess exactly the same optical ellipsoid, orientated in the same manner', and since the form and position of this ellipsoid are thus characteristic of perovskite, the internal structure of the crystals must be orthorhombic and not cubic.

Inasmuch as the observations described below tend to confirm the correctness in essential points of the explanation given by Baumhauer, the relations which should exist between the etching figures on the cube-faces and the orientation of the indicatrix, in the different portions of crystals twinned in accordance with it, are given for reference in figs. 1 and 2.

The specimens of perovskite hitherto described from the Tyrol have been found to differ markedly from the above, both in structure and optical properties. They are three in number, viz.:—

[1] G. Tschermak, Min. Petr. Mitt., 1882, vol. v, p. 194.

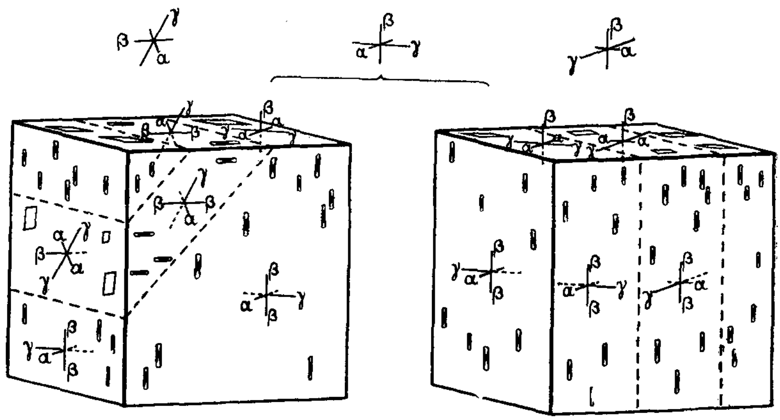
[2] A. Ben Saude, loc. cit., p. 15. It seems possible, however, that this behaviour of the lamella might occur in a polymorphous crystal, in which cracks existed before the change of state.

[3] E. Mallard, Bull. Soc. franç. Min., 1882, vol. v, p. 234.

I. A single small crystal 'from the Wildkreuzjoch', described by Hessenberg in 1861,[1] and examined later optically by himself and von Fritsch,[2] by Des Cloizeaux,[3] and by Klein.[4]

II. A few small crystals on a chip of rock, probably from the same locality, described by vom Rath[5] and by Hessenberg,[6] but not optically examined.

III. Small crystals of 'perovskite from Pfitsch', examined by Klein.[7]



Perovskite: orthorhombic combination {110} {001} showing etching figures and orientation of the axes of the indicatrix.
Fig. 1.—Twinned on (1$\bar{1}$1). Fig. 2.—Twinned on (1$\bar{1}$0).

These all showed cubic forms, like other specimens of perovskite, but had a *diagonal* lamellation only, and were optically biaxial with a positive acute bisectrix of narrow angle perpendicular to the faces of the cube. It was suggested by Ben Saude that the crystal I might not really be perovskite; but crystals from III were found by Klein to have—at least qualitatively—the composition of that mineral. The optical characters of these crystals were interpreted by Mallard,[8] as due to the crossing of lamellae of the more ordinary variety of perovskite.

[1] F. Hessenberg, Abhandl. Senckenberg. naturf. Ges., 1862, vol. iv, p. 20.
[2] F. Hessenberg, ibid., 1872, vol. viii, p. 38.
[3] A. Des Cloizeaux, Neues Jahrb. Min., 1877, p. 160.
[4] In Ben Saude, loc. cit., p. 33 (note).
[5] G. vom Rath, Ann. Phys. Chem. (Poggendorff), 1872, ser. 5, vol. xxiv, p. 595.
[6] F. Hessenberg, Abhandl. Senckenberg. naturf. Ges., 1872, vol. viii, p. 407.
[7] C. Klein, Neues Jahrb. Min., 1884, vol. i, p. 245.
[8] E. Mallard, Bull. Soc. franc. Min., 1886, vol. ix. p. 60.

The problem presented by perovskite falls naturally into two parts:—

(1) The determination of the system to which the substance belongs—whether it is cubic, as indicated by its form, the birefringence being due to strain; or forms mimetic crystals built up of lamellae of lower symmetry corresponding with the optical characters.

(2) The discovery of the causes which have brought about this discrepancy between the form and the optical characters.

In the present paper, the first only of these questions has been considered.

II. Perovskite from the Burgumer Alp.

Some of the chief difficulties hitherto encountered in the determination of the optical properties of perovskite, have been due to the imperfect transparency of the crystals coupled with their complex lamellated structure.

The object of the present paper is to describe the characters observed in a series of exceptionally good and transparent crystals from the Burgumer Alp in the Pfitschthal, Tyrol, which were kindly placed at the author's disposal by Professor P. von Groth, in whose laboratory the earlier portion of the work was carried out.

The Burgumer Alp lies at the foot of the Wildkreuzjoch, and blocks of rock are often found there which have fallen from above. Hence 'Burgumer Alp' must be taken to indicate the same place of origin as 'Wildkreuzjoch', the locality given for the crystal described by Hessenberg. In view of this fact, the differences between the crystals here described and those of Hessenberg, vom Rath, and Klein, are the more remarkable.

The crystals are cubic in habit—often somewhat irregular, owing to the parallel growth of two or more smaller cubes, or cavernous—dark brown, and brilliant; and the largest examined was about $2\frac{1}{2}$ mm. in its greatest dimension. Besides the cube, the dodecahedron is frequently present, and small faces of the octahedron also occur. There are also a number of other forms, but, owing to the striated nature of the faces, they cannot be determined with any certainty. On one crystal a large face, near the dodecahedron, to be referred to later, makes an angle of about 33° with a cube-face, and may belong to the form g {320} which has been previously observed on perovskite (100 : 320 = 33° 41′).

The cube-faces generally show sharp, straight striae, parallel to one or other of their edges, those on different parts of the face being mutually perpendicular. On some crystals the two sets meet along a diagonal line. Dodecahedron-faces also are often crossed by two sets of lines at right angles, parallel and perpendicular to their intersections with the cube.

After measurement, several of the crystals were etched by immersion for $1\frac{1}{2}$ hours in dilute hydrofluoric acid, and the faces examined by reflected light under a magnifying power of 450 diameters. For this purpose a Zeiss 16 mm. (Ap. 0·30) objective and deep eyepiece (Zeiss 18, 10 mm.) were used, as with this arrangement the working distance is sufficiently long to allow the crystal, mounted in a slightly inclined position on a horixontal axis on the stage, to be illuminated directly by daylight.

The pits produced on the cube-faces are seen to be of two types: (1) square or rhomb-shaped, (2) elongated or linear, and the faces are mapped out into areas of two kinds distinguished by the shape of their pits. On most of the plates examined (cf. fig. 3), areas with pits of type (1) were predominant, usually with more or less irregular or wedge-shaped strips showing linear pits scattered through them (as at *b*, *c*). Some few, however, were almost entirely occupied by linear pits (cf. fig. 7).

Drawings were made of the best faces, to show the distribution of the pits, and the crystals were then sliced parallel to these faces, in such a way as to preserve the etched surface for examination by transmitted light.[1]

The plates, which are from 0·2 to 0·7 mm. thick, appear quite transparent (except where flawed) and of a light brown colour, and are excellently suited for optical examination under the microscope. Nine plates in all were prepared, of which seven were parallel to cube-faces, while two were respectively parallel to an octahedron-face and to the face (320) ? mentioned above.

Plates parallel to faces of the cube.

Division into dissimilar areas.—On examination of plates parallel to cube-faces, under the microscope between crossed nicols, two kinds of areas are at once distinguishable, viz.:—

(1) areas showing no interference-colour, extinguishing perfectly at about 45° to the cube-edges, but giving no interference-figure in convergent light;

[1] This work was carried out very skilfully by Messrs. Voigt and Hochgesang of Göttingen.

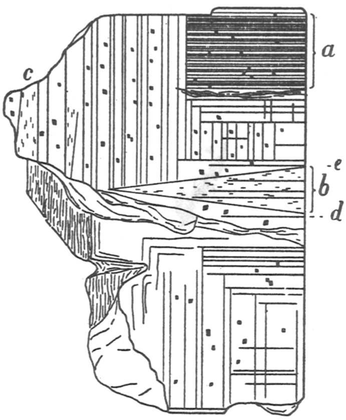
(2) areas showing colours of low order, and in convergent light a single, biaxial optic axis perpendicular to the face. The interference-figure is very well defined, and shows strong axial dispersion, the brush being coloured red on the positive side of the figure. The direction of the brush indicates that the plane of the optic axes is parallel to a cube-edge.

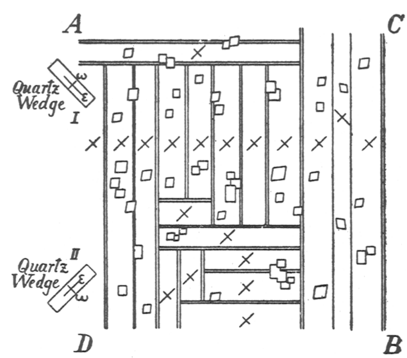
These areas coincide with those defined by the etching figures; rhombic or rectangular pits being found on the former (1), while linear pits occur on the latter (2). These two kinds of areas will be hereafter referred to by the letters *C* and *M* respectively. Thus:

M-areas have linear pits, and are perpendicular to an optic axis;

C-areas have rhombic or rectangular pits, and extinguish at 45°.

A typical plate of this kind is shown in fig. 3.





Perovskite: plates parallel to cube-faces.

Fig. 3.—Showing *C*- and *M*-areas, with cubic lamellae and oblique *C*-*M*-junctions.

Fig. 4.—Arrangement of bands and etching pits on *C*-area.

By the help of the stage-goniometer designed by Professor Miers,[1] the junctions between the *C*- and *M*-areas may be traced across an edge, and the relations of the pits on adjacent cube-faces determined. An *M*-area, whose pits are parallel to the edge, is found to have a similar *M*-area adjacent to it; while an *M*-area, whose pits are perpendicular to the edge, has a *C*-area adjacent to it, and vice versa.

Lamellation of C-areas.—The *C*-areas are almost always divided into broad strips by strongly marked lines or narrow bands parallel to the

[1] See H. A. Miers, 'Mineralogy'. 1902, fig. 364, p. 173.

cube-edges. These are of the same colour as the broad strips, but usually appear brighter, and change in brightness when the mirror is moved so as to give oblique illumination, while at the same time the adjacent broad strips develop a remarkable fluted appearance. The narrow bands have the appearance of thin plates of dissimilar material, about 0·001 to 0·003 mm. thick, arranged parallel to the cube-faces and perpendicular to the surface of the plate (cf. fig. 4). The width of the broad strips varies up to about 0·2 mm. Rarely, a *C*-area is almost entirely free from lamellae (as at *a*, fig. 7).

On inserting a quartz-wedge[1] along one of the cube-diagonals, a section (fig. 3) of 0·624 mm. thickness shows compensation on a *C*-area at about the eighteenth order, indicating a birefringence of about 0·017 for sodium-light. The whole of the area is usually compensated at the same time, when the quartz-wedge is inserted along *AB* (position I, in fig. 4), while the insertion of the quartz-wedge in the rectangular direction along *CD* (position II) causes no change of appearance. In a few cases, however, a narrow strip, parallel to the bands mentioned above, shows compensation in position II, at right angles to that of the broad strips (fig. 4). When pits occur on such a strip, they have not the same orientation as those on the broad strips adjacent, but are arranged symmetrically with respect to the line of contact, as explained below. Thus, as regards compensation and etching, these narrow strips have the character of lamellae in twin-position with respect to the rest of the area, the twin-plane being parallel to a face of the cube (cf. fig. 2).

Form and orientation of etching pits on C-areas.—The etching pits on the *C*-areas are seen to vary in outline—even on the same strip (fig. 4). The smaller ones, which are very well defined, and appear transparent, with flat bottoms, are always clearly rhombic in outline; while the larger ones, which are bounded by four faces of a pyramid and are often opaque, are frequently square or rectangular.

The pits observed by Baumhauer and Ben Saude on similar areas were described as rhombic, either with one pair of sides parallel to the cube-edge (Ben Saude) or with their diagonals parallel to those of the cube-face (Baumhauer). A variation in form somewhat similar to the above seems, however, to have been noticed by Baumhauer on crystals from the Nikolaje Maximilianovskoi mine.[2]

In order to determine the true form and orientation of the pits,

[1] Cut with its length parallel to the axis of the quartz crystal.

[2] H. Baumhauer, Zeits. Kryst. Min., 1880, vol. iv, p. 197.

a number of the sharpest were drawn by means of a Zeiss-Abbe drawing apparatus, with a magnification of about 1,300 diameters. The figures thus obtained were from 5 to 10 mm. in breadth. Each edge was drawn several times in succession with the help of a small straight-edge laid along it, and only those drawings were measured which appeared satisfactory as regards parallelism of the successive lines and of opposite edges. The sides of eight of the best figures were produced, and the angle between them bisected. The inclination of the edge of the pits to the side of the strip was then found to vary from $-\frac{1}{4}°$ to $+7\frac{1}{2}°$, while that of the bisecting lines (or diagonals of the rhombs) only varied between $44\frac{1}{2}°$ and $46\frac{1}{2}°$. Thus, while the angles of the pits vary between 88° and 75°, their diagonals do not deviate from the diagonals of the cube-face by more than $1\frac{1}{2}°$—an amount which, in view of the difficulty of measuring such small figures, probably does not exceed the errors of measurement. The symmetry of all the pits would therefore appear to be the same, notwithstanding their difference in form.

On a few of the narrow strips which are compensated in the second position, etching pits have been observed, and found to have their longer diagonals in the reversed position (fig. 4). It is difficult to get reliable measurements, owing to the rarity of the twinned lamellae which show pits; but in the single case measured the inclination of an edge of the pits to the edge of the lamella was :—

for two pits in the normal position $+5\frac{1}{2}°$ and $+8\frac{1}{2}°$;
for a pit on the twin-lamella $-5\frac{1}{4}°$.

The inclinations of the corresponding diagonals were, respectively, 45°, 43°, and $41\frac{1}{2}°$.

Compensation by the quartz-wedge always occurs when the wedge is inserted along the shorter diagonal of the rhombic pits.

Nature of the narrow bands on C-areas.—The fluted appearance, mentioned above as noticeable when the plate is illuminated obliquely, is seen equally well after removing the analyser, provided that the principal plane of the polarizer is parallel to the plane of vibration of the ray most strongly refracted by the plate. This suggested that the appearance might be caused by total reflection at the surface of the thin sheets, and that these might possibly be only lamellae in twin-position, like the others, but too thin to show compensation by the quartz-wedge.

In order to test this assumption, a plate (fig. 3) was mounted on a goniometer with its own plane and the trace of the lamellae parallel to the turning-axis, and examined in a beam of parallel light from a collimator, by means of a microscope fixed opposite the collimator, the plane of vibration of the light being controlled by a nicol prism. Starting with the plate perpendicular to the line of sight (and the plane of the lamella, consequently, parallel to this line) the whole area appeared bright. On rotating it (in either direction), the appearances varied according to the plane of vibration of the light.

(1) If this plane was parallel to the plane of vibration of the *most* strongly refracted ray in the broad strips, a dark shadow (causing the fluted appearance) appeared on one side of the lamella, increased in width, became reddish, and finally vanished, the whole area becoming again transparent.

(2) If it was parallel to the plane of vibration of the *least* strongly

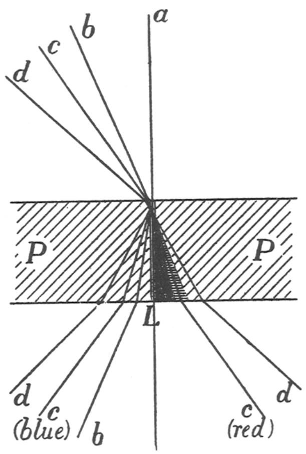


Fig. 5.—Total reflection of light by twin-lamella of low refractive index.

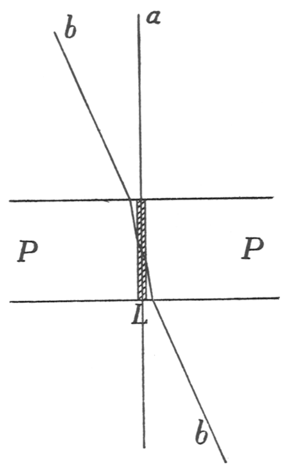


Fig. 6.—Transmission of light through twin-lamella of high refractive index.

refracted ray, no shadows appeared, and the plate remained bright throughout.

The effects to be expected from total reflection from a twin-lamella may be seen from figs. 5 and 6. Let *PP* represent a section of the crystal-plate by a plane perpendicular to the turning-axis, and *L* a twin-lamella; and let the direction of the incident light as the crystal is rotated be, successively, *a*, *b*, *c*, *d*.

If the nicol prism be so set that the refractive index of the plate is higher than that of the lamella (fig. 5), rays parallel to *b* will be reflected by the latter, which will cast a shadow. Of the light incident along *c*, the blue will be totally reflected, while the red will pass through, and the shadow cast will appear red. For an angle of incidence corresponding to d, all colours will be transmitted.

If, however, the refractive index of the lamella is higher than that of the plate, there will be no total reflection (except for rays incident on the outcrop of the lamella, which may be neglected[1]) and no shadow will be cast.

Thus, the observations agree with the assumption that the narrow bands visible in C-areas are lamellae of the same material as the rest of the crystal, in twin-position about a plane perpendicular to C and parallel to the faces of the cube, and differing only in width from the broad lamellae showing etching pits.[2]

By way of verification, when the plate was set to give red shadows, the microscope was turned so as to view the rays reflected from the lamellae, and the light was found to be blue and polarized, the vibrations being in the direction corresponding to the maximum refractive index of the broad strips.

Etching pits on M-areas.—Under a magnification of 1,400 diameters, the linear etching pits are seen to have the form shown in fig. 7, *A–D*. They are bounded by four sloping triangular faces, of which the two lateral ones appear dark, while those at the ends are transparent. The ends of the pits, which are rounded and difficult to see, owing to the slight inclination of the faces, are sometimes at right angles to the length of the pit (as at A), and sometimes inclined to it (as at B and C), indicating the presence of not more than one plane of symmetry perpendicular to the plate. Occasionally the two ends are inclined in the *same* direction, as at D; in which case there would be no plane of symmetry. All these forms may occur on the same homogeneous lamella.

A cube-face showing linear pits over the greater part of its surface is sometimes traversed by a diagonal line of junction, on either side of which the pits are mutually at right angles (fig. 7). A uniform M-area with pits parallel to one cube-edge occasionally encloses a narrow diagonal strip with linear pits parallel to the other edge. The plane of contact appears, on altering the focus, to be perpendicular to the surface of the plate.

[1] Slightly oblique rays falling on the outcrop, would be repeatedly reflected internally through the lamella to emerge at the other side of the plate, and might account for the extra brightness of the narrow bands noticed on p. 164, and for their failure to show compensation.

[2] This has since been confirmed by the discovery of minute rhombic pits in twin-position on a few of the narrow bands.

On M-areas there are also frequently seen narrow straight bands, similar to those on C-areas, running parallel to the linear pits. These are also shown in fig. 7, where the solid lines indicate bands which are in focus at the same time as the pits, and consequently crop out at the surface, while the dotted lines indicate bands which are sunk below the surface of the plate. These bands also represent lamellae perpendicular to the cube-face, as is evident on altering the focus or on tracing them across the edge on to an adjacent cube-face, where they are seen to be identical with the narrow bands on the C-areas. Whether emerging at the surface or not, these are all sensibly parallel to each other within the errors of observation, as are also the diagonal lamellae. In the crystal represented in fig. 7, the angles between the vertical, diagonal, and

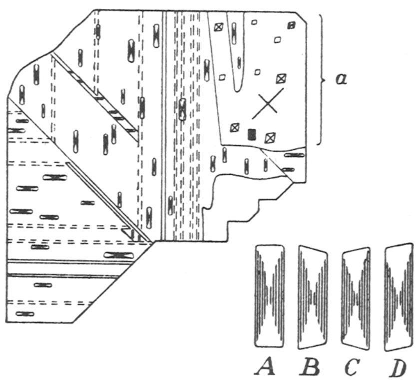


Fig. 7.—Perovskite: plate parallel to cube-face, showing oblique junction of M- and C-areas, and cubic and diagonal lamellae. A–D, forms of etching figures on M-areas.

horizontal lamellae do not differ from 45°, on the average by more than $\frac{1}{2}$°.

On examining a plate of this kind in parallel light from a collimator, as described above, the diagonal junctions and lamellae, as well as those parallel to the cube-edges, show no sign of total reflection when the crystal is rotated, and are almost invisible except between crossed nicols. This is sufficiently accounted for by the fact that an optic axis is normal to the M-areas, so that for rays at a slight inclination to this direction the refractive indices of the two sets of lamellae would be nearly equal.

Junctions between C- and M-areas.—Where an M-area is in contact with a C-area, the line of junction is commonly not quite parallel to a cube-edge, but inclined to it at an angle varying from $4\frac{1}{2}°$ to 8°, the inclination being always towards the shorter diagonal of the rhombic pits on the *C*-area (figs. 3, 7, and 8). In a few cases, however, apparently parallel junctions have been observed (fig. 8, at *z*).

Examination in convergent light.—The interference-figure seen through the *M*-areas in convergent light is quite constant and characteristic; consisting of the well-defined circular rings, in the centre of the field, and straight black brush with strongly coloured edges, which indicate the perpendicular emergence of an optic axis of a biaxial crystal with wide axial angle and considerable axial dispersion. The plane of the optic axes is in all cases perpendicular to the length of the linear etching pits. The brush is coloured red on the side towards the positive bisectrix. The colours are usually on the same sides of the brush over the whole of an *M*-area, but here and there a strip may show them in the reversed position, as they would be in a lamella in twin position about a cube-face. This is in accordance with the observed uniform character of the *C*-areas, in which only occasional strips (other than the narrow bands) occur in twin position.

On examining in convergent light a *C*-area fairly free from fine lamellation and showing uniform extinction, two brushes sweep symmetrically across the field, meeting in the centre (as they would do in a plate of crystal perpendicular to a third mean line); but even with sodium-light no interference-bands are visible, although the plate may be perfectly transparent, and (but for the lamellae) apparently homogeneous.

On tilting the plate in a plane containing its normal and one of its extinction-lines, i. e. in a plane parallel to a cube-diagonal, no bands come into view, and owing to the narrowness of the lamellae the light is soon cut off by total reflection. Even on tilting in a plane parallel to one of its edges, so as to bring one of the optic axes towards the line of sight, no rings become visible.

An attempt was made to eliminate any disturbance caused by lamellae by selecting a small fragment of an etched crystal, as free as possible from them, and grinding it down into a small rectangular prism about $\frac{1}{2}$ mm. in length, bounded by three natural cube-faces (in a zone), one of which showed linear pits, and three polished surfaces.

When mounted on the stage-goniometer, the etched face, and that next it, showed in convergent light each a perfectly normal interference-figure corresponding to a biaxial optic axis emerging perpendicularly. Similar figures were visible through the parallel faces, on rotating the prism.

All the optic axes showed strong dispersion, the brush being strongly coloured (red and blue) on its edges, and the red being always on the positive side of the figure. The appearance and relations of the four figures was quite normal, and there was no indication of a dispersion of the bisectrices which would indicate less than orthorhombic symmetry. In the intermediate positions, however, in which the bisectrices should have been visible, the figure always disappeared and no figure corresponding to a bisectrix could be seen. This may perhaps have been due to the high refractive index (about 2·4),[1] which would cause a considerable amount of refraction (or total reflection) at the corner of the crystal, even when the latter was immersed in cedar oil ($\mu = 1{\cdot}516$); or it may possibly be due to a few lamellae, traces of which were visible through the faces parallel to the axial plane. Through the pair of faces parallel to the axial plane, two symmetrical brushes, but no interference-bands, are visible in sodium-light.

The *C*-area marked *a* in the corner of the plate shown in fig. 7, which appears to be quite free from lamellae, was also examined on the stage-goniometer under the microscope. When the plate is horizontal, it shows a pink of the fifth order, and this colour does not change when the plate is inclined as much as 60° in either direction, which would correspond to an inclination of the ray within the crystal of about 21° to the plate-normal. In convergent sodium-light no rings are visible, but when the plate is horizontal two ill-defined brushes appear to meet symmetrically in the centre of the field.

The form and relative orientation of the etching pits, as well as the optical characters of the plates parallel to the cube, as observed above, are in accordance with Baumhauer's view; but, as will be seen on comparing figure 1 with figures 3 and 7, the linear pits do not lie at right angles to the junction between *C*- and *M*-areas (as in fig. 1) but in all cases (approximately) parallel to them. This point will be referred to later (p. 173).

Plate parallel to g (320)?

A plate cut parallel to the face *g* (320) (cubic form) mentioned on p. 161, shows through the greater part of that face a series of parallel strips, inclined at about 10° to its intersection with the cube, as shown in fig. 8. The vertically shaded portions of the face *g* show definite extinction in the direction of the lines of shading, and, with convergent

[1] As determined by means of a prism of about 45° made by polishing a cube- and a dodecahedron-face on the same small fragment.

light, the emergence of a negative bisectrix of wide axial angle, the optic axial plane being horizontal, and the bisectrix inclined somewhat to the face-normal in that plane. These appearances agree with the assumption of an optic axis emerging perpendicular to each of the adjacent cube-faces, the bisectrix being perpendicular to the face of the dodecahedron; and on turning the crystal so that the face *m′* is horizontal an optic axial figure of the usual type is visible, the brush being coloured blue on the side towards the negative bisectrix, as in other cases. When *g* is horizontal, the shaded portions of the adjacent cube-faces, *m* and *m′*, also show extinction along the lines of shading.

The strips are the outcrops of lamellae, which, on rotating the crystal, are seen to dip into the face *g* at about 68°. The junctions can be traced across the edges on to the triangular face *d*, and further on to the cube-face *c*, on which (though rather indistinct) they appear to run parallel to the edge *c*/*m*. On the face *m′* they make an angle of 8° with the cube-edge, and the lamellae are consequently parallel to a plane in the zone [*cm*], inclined at about 8° to *m*. The traces upon *c* of a few of the junctions, however, are slightly inclined (10°–12°) to the edge *c*/*m*.

The alternate strips on *g* show two types of etching figures, *A* and *B*. Those parts of the face which are shaded exhibit pits resembling *A*, while on other parts the pits are of type *B*, though some (near *p*) are much more elongated. The relations of these pits to each other and to those on the adjacent cube-faces are as indicated in the figure. The orientation of each type is the same throughout.

The lamella *r* is sufficiently thick to intersect both the face *g* and the cube-face *m′*. On the former it shows *A*-pits, and on the latter vertical linear pits (*M*-area) and a normally emergent optic axis, as mentioned above.

On the cube-face, at *t*, is a strip of *C*-area, representing the outcrop of a lamella parallel to the others, and showing the same relation to the adjacent *M*-areas as was previously described (p. 168). But at *z* are some small *C*- and *M*-strips whose junctions are *parallel* to the cube-edges.

At *v* are seen pits of type *B*, and on the adjacent cube-face, at *w*, the pits are rhombic (*C*-area), the relative orientations being as shown. The areas *v* and *w* appear to belong to a single lamella.

The relation between the rhombic pits at *x* and the *B*-pits shown at *p* is incompatible with that of the pits at *v*, *w*. This point is referred to below (p. 174).

Some of the lamellae (such as *r*, *s*, *t*) enclose narrow bands parallel to the cube-edge, and evidently identical with those seen in plates parallel to cube-faces.

Plate parallel to an octahedron-face.

A plate parallel to an octahedron-face on the corner of a cube with truncated edges, shows on that face monosymmetric etching pits of the form and orientation indicated in fig. 9. The face is surrounded by

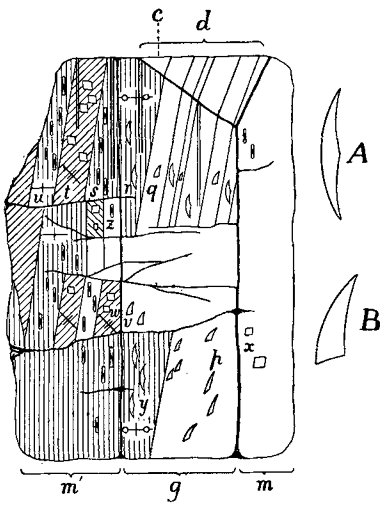


Fig. 8.—Perovskite : plate parallel to g (320), showing lamellae and etching figures upon g and upon the adjacent cube-faces.

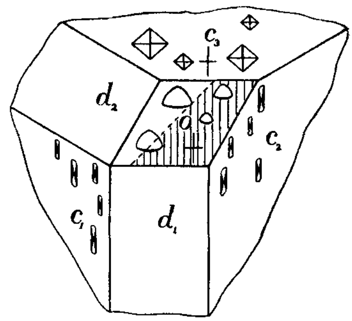


Fig. 9.—Perovskite : section (free from lamellae), parallel to octahedron-face (o), showing etching figures upon o and upon the adjacent cube-faces.

three faces of the cube and two of the dodecahedron, indicated by the letters c and d respectively.

With transmitted light the plate shows extinction, on the shaded portion, parallel to the lines of shading, and is compensated by a quartz-wedge at right angles to these lines. The want of extinction on the unshaded portion is due to a subjacent layer near the under surface of the plate.

The whole face, and the parts of the surrounding faces adjacent to it, appear uniform and free from lamellae. The dodecahedron-faces show no clear pits, but the three cube-faces exhibit well-defined pits of the forms shown. Of the two former, d_1 is bright, but d_2 rough with crossing furrows.

The angles between the faces of this crystal were measured on the goniometer, with the help of the attachment described in the succeeding paper. Sharp reflections were obtained from the faces c_2, c_3, o; and c_1, though vertically striated, gave a reliable reading in the zone $[c_1c_3]$. The following values were obtained: $c_1 c_3$ 89° 55′, $c_2 c_3$ 89° 58′; oc_3 54° 35′, oc_2 54° 38′.

III. Discussion of Results.

It will be seen that the crystals from the Burgumer Alp agree closely in their structure and optical characters with those from Zermatt and the Urals described by Baumhauer and (except in the orientation of the rhombic pits) by Ben Saude, and do not show any of the peculiarities previously found in crystals from this locality.

The definiteness and regularity of the structure and etching figures, and of the optical characters, together with the constant relations existing between them, appear to the author to exclude the possibility of their being caused by strain in a cubic material, and to indicate that the crystals really belong to one of the biaxial systems—most probably to the orthorhombic system, as supposed by Des Cloizeaux and by Baumhauer. The detailed explanation, indeed, proposed by the latter (p. 158), appears sufficient to account for almost all the phenomena observed in the crystals above described, as well as those of the crystals from Zermatt and the Urals, as may be seen on comparing the description with the figures given on p. 160.

The fact that in plates parallel to the cube-faces, which show *C*- and *M*-areas in contact with one another, the linear pits are parallel to the line of junction (or nearly so) instead of perpendicular thereto, as described on p. 170, might be explained on the supposition that the crystals, while in twin position about (111), are not in contact along this face but along a plane near $(1\bar{1}0)$; but the relation may be more naturally expressed as resulting from a rotation through one quarter-turn about the pseudo-tetragonal axis perpendicular to (110), on the principle laid down by Mallard. The contact is usually along a plane slightly inclined to the cube-face, the lines of junction of the *C*- and *M*-areas being inclined to the cube-edge, in the direction of the shorter diagonal of the rhombic pits, at angles which vary between $4\frac{1}{2}$° and 8°, but occasionally (on the crystal shown in fig. 8) are zero.

The plane of contact does not appear to have rational indices (in which respect it resembles the 'plane of rhombic section' of the plagioclase felspars), or even to lie in a definite zone, as the inclination of its traces on two adjacent faces of the cube is not necessarily the same. In this case the plane bears a different relation to the two individuals. The constant parallelism of narrow bands occurring in lamellae with this kind of contact (as in fig. 3, *b*, *d*, *e*, and fig. 8, *r*, *s*, *t*) shows, however, that the twin relation is always the same and is independent of the direction of the plane of contact.

Although none of the plates examined have shown linear pits at right angles to a *C*-*M* junction, the occurrence of diagonal junctions, with pits mutually perpendicular on the two sides, and the plane of contact apparently perpendicular to the cube-face (as in fig. 7), can only be accounted for by the assumption of twinning on a face of {111} with contact along the twin-plane, as described by Baumhauer.

The twinning observed is thus precisely what might be expected to occur in a pseudo-cubic substance, viz. twinning by (i) one half, or (ii) one quarter-turn about the pseudo-tetragonal axis perpendicular to *M* (110), contact in (i) being along (110) and in (ii) along a plane slightly inclined to this face; (iii) one half-turn about the pseudo-digonal axis perpendicular to (111), with contact along this face.

As regards the etching figures on faces other than those of the cube, which have not been previously described, it may be pointed out that of the pits observed on the face *g* (fig. 8), those of the form of *B*, which are adjacent to a cube-face having rhombic pits, show the absence of symmetry proper to a face of an orthorhombic pyramid. Those having the form of *A*, which are adjacent to a cube-face with linear pits, have the monosymmetric character proper to the faces of an orthorhombic prism. The indices of this would be {510}.

If we admit that the areas *v* and *w* belong to the same lamella, the relation between the various areas on this crystal are in accordance with the laws of twinning stated above. Thus the lamellae *r*, *s*, *u*, &c., would be in parallel position and separated by the lamellae *t*, *q*, &c., in twin position. The discrepancy between the relation at *vw*, and that at *px* might be due to the existence of a twin junction between *p* and *x*, with twin-plane parallel to that face of {111} which is nearly perpendicular to *p*, or possibly to the fact that since the angle *mg* (56°) is not equal to *m′g* (33°), the area at *p* would represent a different form from that at *v*, and might therefore naturally have different pits. The indices of the various areas would be as follows: *twx* {001}, *su*

{110}, *ry* {510}, *qv* {223}, *p* {332}. Unfortunately this part of the crystal was damaged, so that this question could not be settled.

The evidence for orthorhombic symmetry afforded by the etching figures and optical characters of the crystal-corner shown in fig. 9, which is unusually free from complication by lamellae, is, however, particularly striking. The characters are, in fact, precisely those which should be found in an orthorhombic combination of (001), (110), ($\bar{1}$10), and (021).

On the other hand, though it is hardly justifiable to draw conclusions from a single crystal, it should be noted that while the angles c_1c_3 and c_2c_3 (fig. 9) are very nearly 90°, the angles oc_3 and oc_2 differ considerably from the cubic angle, (100) : (111)=54° 44′. The angle oc_1 would therefore also be different, and would not be equal to oc_2. If this difference should be confirmed, the symmetry could not be orthorhombic.

It may also be mentioned that on a very finely lamellated *C*-area, at *a* in fig. 3, which consists of alternate lamellae of about equal breadth in twin position, the lamellae are not extinguished simultaneously at exactly 45° to the cube-edges, but in two sets, as in a plagioclase felspar; and that the extinction-positions of these are not symmetrical to the junctions (cube-edges), the measured angles being 42½° and 48° respectively. This again would, if confirmed, indicate that the symmetry is less than orthorhombic; and the same is true of the etching pits of the form *D* (fig. 7).

It is thus possible that perovskite may ultimately have to be referred to the monoclinic or anorthic system; but so many of its characters point to orthorhombic symmetry that it may for the present be considered to belong to that system.

The absence of interference-bands from *C*-areas does not appear to be due to the overlapping of layers in non-parallel position, since it is noticeable in thin as well as in thick plates.

The crystalline characters of perovskite may be shortly stated as follows:—

System: Orthorhombic ? (pseudo-cubic).

$a:b:c=1:1:0{\cdot}7071.$

Principal forms: *M*{110}, *C*{001} = 'cube.'

a{100}, *b*{010}, {111} = 'dodecahedron.

{201}, {021} = 'octahedron.'

{510}, {223}, {332} (?).

The crystals always show a lamellated structure due to twinning, (i) by a half-turn about the normal to (110), (ii) by a quarter-turn about the same line, (iii) by a half-turn about the normal to (111).

Plane of the optic axes parallel to $C(001)$. $2V=90^{\circ}$ (about). Negative bisectrix (α) perpendicular to (100). Dispersion of the optic axes, strong; about the positive bisectrix $\rho > v$. Birefringence moderate, $(\gamma-\alpha)=0{\cdot}017$ (measured by compensation of a plate with rhombic pits; see p. 164).

With regard to the cause of the cubic form, the lamellated structure at once recalls that of leucite, and suggests strongly that, like it, perovskite may be dimorphous. This explanation has already been proposed by several authors; but, so far, there is no direct evidence of the existence of a cubic variety of perovskite.

Ben Saude, indeed, noticed that after heating to redness the outline of the optically dissimilar areas had slightly changed.[1] This might have been due to dimorphism; but similar changes of twin-structure have been observed to take place in polysymmetric substances—as potassium sulphate—without change of state. On the other hand, Brauns [2] found that no difference could be detected in the optical properties of a crystal, of which one-half was heated to redness.

As an argument against the existence of polymorphism in perovskite, Ben Saude mentions the fact, noticed by Hautefeuille, that artificially prepared crystals are doubly refracting. It seems quite possible, however, that a change of state might occur during the process of cooling of crystals which were originally cubic, at the temperature and under the conditions of formation.

In conclusion, the author desires to express his gratitude to Professor von Groth, at whose instance the work was undertaken, for the loan of the material and for much kindly interest and advice while he was working in his laboratory in Munich.

[1] Loc. cit., p. 27. The fact that on the areas which had suffered change by heating the pits remained unaltered in form, was mentioned by Ben Saude as showing the unsuitability of etching figures for the determination of symmetry. Since, however, the pits only indicate the nature of the structure existing at the time when they were formed, they could not (as has been pointed out by Ewing, Proc. Roy. Soc., 1900, vol. lxvii, pp. 112–117, in the case of etched surfaces of metals) change their shape owing to a subsequent alteration of that structure. Had the crystals been re-etched, there can be little doubt that the new figures would have tallied with the altered optical properties.

[2] R. Brauns, 'Die optischen Anomalien der Krystalle.' 1891, p. 349.