

*The structure of aragonite.**(With Plate VI.)*

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WE are unable to observe crystalline structure directly, and can only infer it by observation of the physical and chemical properties possessed by a crystal. It is quite reasonable to suppose that every vectorial property possessed by a crystal is dependent upon its *leptonic structure*.<sup>1</sup> The X-ray method, which has produced such a revolutionary change in our knowledge of crystal-structure, is not sufficient in some cases for the determination of leptonic structure. The X-ray spectral analysis gives only the spacings between the atomic planes of a crystal. The application of the method of intensities, which was so successful in the case of simple cubic crystals, may not be so in the case of crystals of a more complex chemical composition and of a lower symmetry. It is thus desirable to combine several methods and so approach the problem from different directions. Unfortunately, at the present time only few relationships between the leptonic structure and the properties possessed by a crystal are well known, and, therefore, the methods available for its determination are also limited.

In this paper, besides constructing a new model of the leptonic structure of aragonite, an attempt is made to introduce a new method for the determination of leptonic structure, which is used in conjunction with some other well-known methods. This is the method of etch-figures.

Etch-figures, up to the present, have been used only to determine

<sup>1</sup> The term 'leptonic' (λεπτός, small, fine) was suggested by F. Rinne (Das feinbauliche Wesen der Materie nach dem Vorbilde der Kristalle. Berlin, 1922. Engl. transl. by W. S. Stiles, London, 1924). [Min. Abstr., vol. 2, p. 414.]

the true crystal-symmetry (amphisymmetry),<sup>1</sup> but it is quite obvious that every etch-figure is determined by the particular arrangement of atoms in the crystal. A true leptonic model must, therefore, explain all the etch-figures produced on the faces of a given crystal.

The present paper consists of a morphological study, a study of the data given by X-rays (a new interpretation of W. L. Bragg's measurements), and a study by means of etch-figures, together with some discussion of the symmetry of aragonite.

### *Morphological Study.*

Aragonite is usually considered to belong to the orthorhombic system, but its true symmetry has been suspected by many mineralogists<sup>2</sup> to be lower than holohedral, and some have even placed it in the monoclinic system.

Having obtained some perfect crystals of aragonite from the Mineralogical Collection of the Hancock Museum at Newcastle-upon-Tyne, the author decided to repeat the goniometric measurements, in order to find out whether any elements of symmetry were missing or their presence doubtful. This particular set consists of ten crystals, numbered 277.15 to 277.24 in the Museum catalogue. They are perfectly transparent and with a slight yellowish tint. The locality is unknown, but it is probable that they came from Bilin, Bohemia. They are of prismatic habit and vary in size from 1.2 to 3.6 cm. All of them are twinned on (110). The majority of them are composed of two well-developed half-individuals united by a very thin lamella, but some are complex polysynthetic twins. The minute thickness of the intervening lamellae makes the twinned crystals appear as simple individuals. In some cases, parallel growth accompanies the twinning and more complex crystals are produced. Nine of these crystals were measured on the no. 2 Fuess reflecting goniometer, and the results for the principal faces are presented below.

Angle.	Observed (mean).	No. of observations.	Calculated (Dana).
(110) : ( $\bar{1}\bar{1}0$ )	68° 49' 40''	9	68° 48'
(110) : (010)	58 5 15	20	58 6
(011) : ( $0\bar{1}\bar{1}$ )	71 38	5	71 32
(010) : (011)	54 13 20	10	54 14
(011) : (012)	16 3	5	15 58

<sup>1</sup> E. T. Wherry, Amphisymmetric crystals. Amer. Journ. Sci., 1922, ser. 5, vol. 4, p. 237. [Min. Abstr., vol. 2, p. 106.]

<sup>2</sup> J. Beckenkamp, F. Wallerant, C. Viola.

All the forms ( $\{010\}$ ,  $\{011\}$ ,  $\{111\}$ ,  $\{012\}$ ,  $\{051\}$ ,  $\{121\}$ ) are holohedrally developed, with the exception of  $\{122\}$ ,  $\{212\}$ , and  $\{031\}$ . It is possible that half of the faces of these forms have been suppressed merely by the conditions of crystal-growth. On the other hand, their hemimorphism may indicate a true hemimorphism with regard to the vertical plane of symmetry (010). The presence or absence of any other elements of symmetry cannot be ascertained from the present morphological study, because of the twinning and the absence of the lower half of the crystals.

*Striations.*—The striations observed on the faces of crystals are usually the traces of certain other faces, which may or may not be developed. In the case of aragonite the striations are developed as follows:

On the face (010)—horizontal. Representing the trace of either (011) or (001).

On the face (011)—horizontal. Trace of (0 $\bar{1}$ 1) or (001).

On the face (110)—inclined at about  $58^\circ$  to the vertical, either towards (100) or (010). Sometimes both striations are present on the same face, either intercrossing one another or in combination. These striations are traces of the following faces:

(a) Inclined towards (010)—trace of (011) or (10 $\bar{1}$ ).

(b) Inclined towards (100)—trace of (101) or (0 $\bar{1}$ 1).

The theoretical angle of the traces of all these planes on the face (110) is  $58^\circ 30'$  measured to the vertical.

J. Beckenkamp,<sup>1</sup> in his work on aragonite, has definitely stated that the striation on (110) indicates the hemimorphism in the direction of the *c*-axis. This was also confirmed by Hankel's<sup>2</sup> investigations of the pyroelectric properties of aragonite. Such a deduction is quite plausible, although the striations on (110) could also be produced by unidirectional crystal-growth. But if we accept the striations as evidence of symmetry, we have to admit the absence of the horizontal plane of symmetry.

Although the morphological characters and striations do not prove quite definitely the absence of a vertical and a horizontal plane of symmetry, they confirm the prevailing doubt about the holohedral nature of aragonite. Sir Henry Miers inserts a question-mark after the word 'holosymmetric' in the description of aragonite in his 'Mineralogy'

<sup>1</sup> J. Beckenkamp, *Zeits. Kryst. Min.*, 1888, vol. 14, p. 376; 1890, vol. 17, p. 321.

<sup>2</sup> W. G. Hankel, *Über die thermoelektrischen Eigenschaften des Aragonites*. Abhand. math.-physischen Cl. Sächs. Gesell. Wiss., 1874, vol. 10, pp. 343–416.

(1902). Beckenkamp and Hankel from their pyroelectric and etching studies concluded that aragonite is hemimorphic with reference to the *b*-axis and *c*-axis, and also that *a* is the only axis of symmetry, while planes of symmetry are absent. The apparently holohedral forms of aragonite were explained by them as due to some complex twinning of simple hemihedral individuals.

According to Wallerant the true symmetry of aragonite is monoclinic, though morphologically it is pseudo-orthorhombic. He also supports the idea of Beckenkamp, that the twinning is the real cause of this pseudo-symmetry. Wallerant was the first to introduce the term 'apparent symmetry' (*la symétrie apparente*), which he applied to those crystals showing a higher morphological symmetry than that shown when other characters are taken into consideration. This term 'apparent symmetry' obviously corresponds to Wherry's 'amphisymmetry'.

'Cette notion de symétrie apparente, qui nous amène à admettre qu'un corps cristallisé peut présenter un axe de symétrie dans ses formes cristallines et même dans son ellipsoïde d'élasticité optique, sans que cet élément se retrouve dans sa structure, est évidemment en contradiction avec les idées reçues, avec les idées courantes. Mais cette conception de la symétrie résulte d'une habitude et n'est justifiée par aucun raisonnement. Il est bien vrai que, si un corps cristallisé possède un axe de symétrie de structure, c'est-à-dire dans son réseau et sa particule complexe, cet axe se retrouvera dans ses formes cristallines et ses propriétés optiques; mais la réciproque n'est pas démontrée, quoique, par habitude, on l'admette sans discussion. Il est, en effet, facile de montrer par quelques exemples que la symétrie peut paraître plus élevée qu'elle ne l'est en réalité.'<sup>1</sup>

The leptonic structure, which we are going to consider here, leads us to a simple solution of apparent symmetry in aragonite, without any invocation of twinning.

#### *The Leptonic Model of Aragonite and its relation to the X-ray spectra.*

The structure of aragonite has already been studied by two authors. M. L. Huggins<sup>2</sup> approached this question from a purely hypothetical point of view, assuming a certain static arrangement of electrons, and, from that, deducing the structure of the crystal. His assumptions are unproved, and even the dimensions of the unit cell do not correspond to those arrived at subsequently by means of X-rays.

<sup>1</sup> F. Wallerant, *Étude sur la forme primitive des corps cristallisés et sur la symétrie apparente*. Bull. Soc. Franç. Min., 1901, vol. 24, p. 194.

<sup>2</sup> M. L. Huggins, *The crystal structures of aragonite (CaCO<sub>3</sub>) and related minerals*. Physical Rev., 1922, vol. 19, p. 354. [Min. Abstr., vol. 2, p. 330.]

Quite recently W. L. Bragg<sup>1</sup> has suggested another leptonic structure for aragonite, based on the X-ray spectra for eight different faces. The spacings calculated are in a perfect agreement with those of the X-ray spectra, but in spite of this fact, no doubt very important in itself, any one closely scrutinizing Bragg's model cannot fail to notice the apparent statical instability of the whole structure. This instability becomes quite clear if we examine the position of the triad group of  $\text{CO}_3$ . This group is placed between six calcium atoms, situated at the corners of a distorted octahedron. The distances from O-atoms to the neighbour-

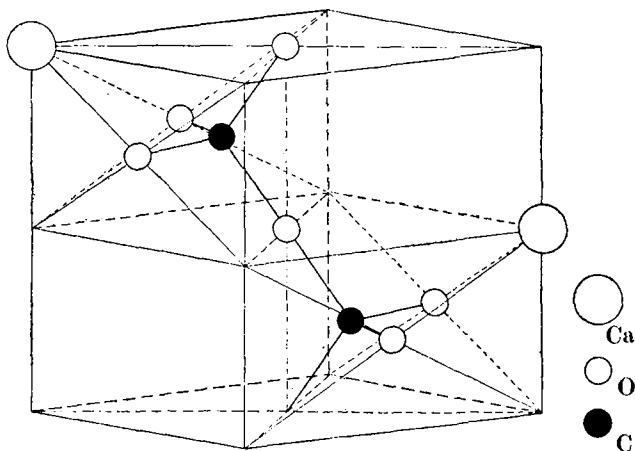


FIG. 1. Orthographic projection of the unit cell of aragonite.

ing Ca-atoms are as follows: 2.28, 2.64, 2.64, 2.47, 2.60, 2.45 Ångström units. Such a variability of atomic distances, especially in the case of analogous points of a homogeneous crystalline assemblage, is hardly possible. After many attempts to bring the triad group in a more stable position, the present author decided to seek another way out of this difficulty.

It is a well-known fact that, on heating, aragonite undergoes a gradual transformation into calcite. Le Chatelier believes this transformation to be endothermic, with a very small latent heat of transformation. This means that the expenditure of energy for the transformation must be very small, and therefore the modification of the respective

<sup>1</sup> W. L. Bragg, The structure of aragonite. Proc. Roy. Soc. London, 1924, ser. A, vol. 105, p. 16. [Min. Abstr., vol. 2, p. 195.]

leptonic structures must be as simple as possible. Hence it was thought that the structure of aragonite might be arrived at by attempting to modify the leptonic structure already known for calcite. The fact that spacings for planes (001) and (100) are identical in both crystals suggests a possibility of a simple leptonic transformation.

A number of leptonic models derived in such a manner were produced. Those which did not agree with the observed X-ray spacings were rejected. Those remaining were subjected to a final test by comparing

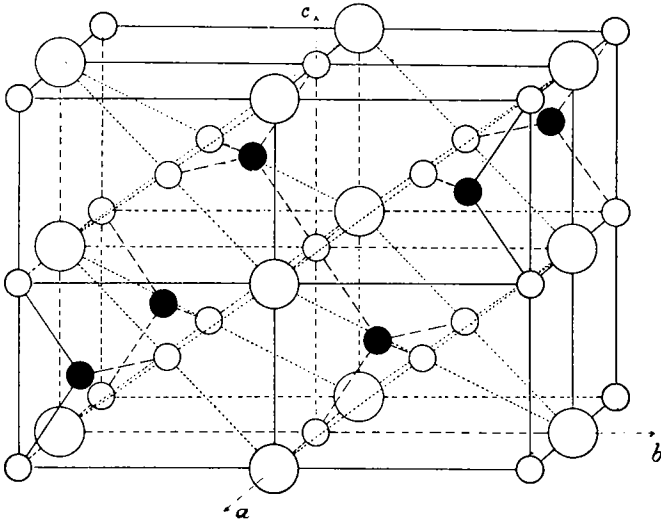


FIG. 2. Orthographic projection of the 'grosser unit' of the aragonite structure. (Same orientation and scale as in fig. 1.)

the reticular structure of each face with the observed etch-figures produced on that particular face. A complete description of this new method of estimating the crystal-structure will be given later. It is important to mention here that the structure finally selected is in perfect agreement with all the etch-figures.

This structure is based on the orthorhombic space-lattice  $\Gamma'_o$ . The unit cell is a rhombic prism (fig. 1), the dimensions of which are taken from the data supplied by W. L. Bragg, and are  $d_a = 2.47$ ,  $d_b = 3.97$ ,  $d_c = 2.86$  Å. Fig. 2 represents the orthographic projection of the 'grosser unit' of this structure, and fig. 3 its projection on the three principal planes. The volume of this 'grosser unit' is  $2d_a \times 2d_b \times 2d_c$

= 224.36 A.<sup>3</sup>. The volume of the unit-cell is 112.18 A.<sup>3</sup>, and, therefore, the 'grosser unit' represented on fig. 2 contains two unit cells. The position of all atoms is clearly seen on the drawings and requires but little explanation. Besides atoms of Ca and O placed at the vertices of the larger rhombic parallelepiped, there are atoms of O placed in the

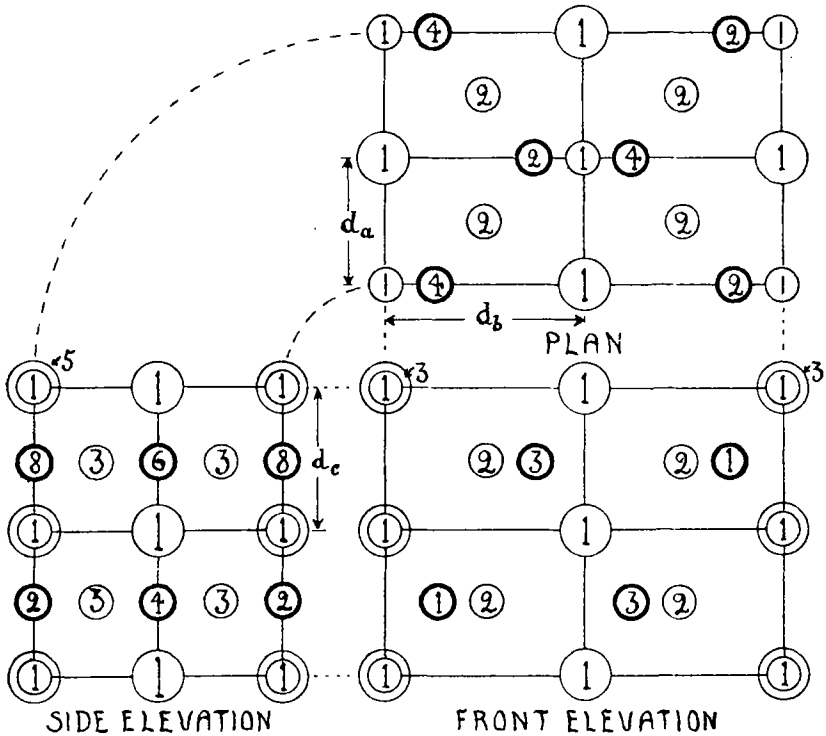


FIG. 3. Projections of the 'grosser unit' of the aragonite structure on the three principal planes (001), (010), (100). (The numbers inside the circles indicate the atomic layers in which the atoms are situated.)

centre of each of the smaller parallelepipeds, and also carbon atoms inside the tetrahedra formed by O-atoms.

The homogeneity of crystalline structure implies that the crystal must be composed of one or many interpenetrating identical lattices, one or more for each kind of atom. This rule is strictly observed in the structure proposed. Altogether there are ten interpenetrating orthorhombic space-lattices. If we take one oxygen lattice as the primitive

lattice and choose one atom as the origin ( $x = 0, y = 0, z = 0$ ), the co-ordinates of analogous points of all lattices will be as follows :

Lattice	$O_{a1}$	...	...	$x = 0$	$y = 0$	$z = 0$
"	$O_{a2}$	...	...	$x = \frac{1}{2}d_a$	$y = 0$	$z = d_c$
"	$O_{\beta 1}$	...	...	$x = \frac{1}{2}d_a$	$y = \frac{1}{2}d_b$	$z = \frac{1}{2}d_c$
"	$O_{\beta 2}$	...	...	$x = \frac{1}{2}d_a$	$y = 1\frac{1}{2}d_b$	$z = \frac{1}{2}d_c$
"	$O_{\beta 3}$	...	...	$x = \frac{1}{2}d_a$	$y = \frac{1}{2}d_b$	$z = 1\frac{1}{2}d_c$
"	$O_{\beta 4}$	...	...	$x = \frac{1}{2}d_a$	$y = 1\frac{1}{2}d_b$	$z = 1\frac{1}{2}d_c$
"	$Ca_1$	...	...	$x = 0$	$y = d_b$	$z = 0$
"	$Ca_2$	...	...	$x = 0$	$y = d_b$	$z = d_c$
"	$C_1$	...	...	$x = 0$	$y = \frac{1}{4}d_b$	$z = \frac{1}{2}d_c$
"	$C_2$	...	...	$x = 0$	$y = \frac{3}{4}d_b$	$z = \frac{3}{2}d_c$

Note.—The Greek letters indicate separate homologous series of lattices of oxygen atoms.  $O_a$  atoms are situated at the vertices of the larger parallelepiped ( $2a \times 2b \times 2c$ ), and the middle of its upper and lower planes;  $O_\beta$  atoms in the centre of the smaller parallelepipeds ( $a \times b \times c$ ).

We may suppose that in aragonite the atoms are held by forces of electri-valency, but the possibility of co-valent links especially in the case of  $CO_4$  leptonic group, is not altogether excluded. If the atoms in a crystal are held together by means of electrostatic charges, then in our leptonic structure we find that all charged atoms (ions) are well balanced. Table I gives the co-ordination numbers and the co-ordinated atoms. The law of Werner finds a confirmation in our case, as the number of co-ordinated atoms (in one shell) does not exceed eight.

TABLE I.

Atoms.	Co-ordination number.	Co-ordinated to atoms.	Atomic distances in Å.	Arrangement.
$O_a$	6	{ 2Ca 4Ca	2.47 3.80	} In plane (010)
$O_\beta$	4	{ 4Ca	2.74	} In plane (110)
Ca	10	{ 20 $a$ 80 $\beta$	2.47 2.74	} Polar axial (axis $a$ ) Parallelepipedal

The position of the carbon atom inside the tetrahedron of oxygen atoms cannot be fixed precisely. From the study of the etch-figures we may suppose that it occupies the position shown in the diagram. In that case the eccentric position of the carbon atom in the tetrahedron may be due to its closer approach to one set of calcium atoms which, being



electro-positive, exert a repulsive action on the electro-positive carbon atom. But we may also suppose that this grouping will try to rearrange itself in such a way as to become more symmetrical, i. e. more stable. These possible minor translations of oxygen atoms would not affect the general structure, although they may greatly modify the intensities of the X-ray spectra.

Having now finished the consideration of the leptonic structure of aragonite, we may examine its relation to the actual X-ray spectra. Table II gives the spacings and intensities of X-ray spectra for eight faces of aragonite as determined by W. L. Bragg, together with the spacings calculated and the structure of each face. From this table we can see a perfect agreement between the calculated and observed spacings for the faces (100), (130), (010), (110), (001), and (101). The two faces (102) and (011) give only half the observed spacing and therefore require special consideration.

TABLE II.

Face.	<i>a</i> calculated.	<i>a</i> observed (W. L. Bragg).	Structure.	Intensity of spectra (W. L. Bragg).					
				1st	2nd	3rd	4th	5th	6th
(100)	2.47	2.47	— CaCO ——— O <sub>2</sub> ——— CaCO —	83	61.5	6.8	4.5	—	—
(102)	1.23	2.47	— CaCO ——— O <sub>2</sub> ——— CaCO —	88	21.5	abs.	—	—	—
(130)	2.32	2.33	$\frac{1}{2}$ C—CaO— $\frac{1}{2}$ C ——— O <sub>2</sub> ——— $\frac{1}{2}$ C—CaO— $\frac{1}{2}$ C	53	37	4	2	—	—
(010)	3.97	3.97	— CaO ——— $\frac{1}{2}$ C ——— O <sub>2</sub> ——— $\frac{1}{2}$ C ——— CaO —	abs.	22.7	17.1	7.7	abs.	4.8
(110)	4.20	4.20	— CaO ——— $\frac{1}{2}$ C ——— O <sub>2</sub> ——— $\frac{1}{2}$ C ——— CaO —	abs.	55	18.6	3.8	1.5	7.1
(011)	2.32	4.64	$\frac{1}{2}$ C—CaO <sub>3</sub> — $\frac{1}{2}$ C ——— ——— $\frac{1}{2}$ C—CaO <sub>3</sub> — $\frac{1}{2}$ C	abs.	54	abs.	3.3	4.9	4.5
(001)	2.86	2.86	— CaO ——— CO <sub>2</sub> ——— CaO —	30	6.2	15	2.3	abs.	—
(101)	1.88	1.87	— CaO <sub>3</sub> ——— ——— CaO <sub>3</sub> —	60	2	2.7	—	—	—

In view of the perfect explanation of the etch-figures of aragonite provided by the leptonic model which has been described above, it appeared undesirable to reject completely the proposed model, notwithstanding the abnormal spacing of those two faces. The explanation of this discrepancy may perhaps be found in the consideration of a new factor, which has apparently escaped the attention of mineralogists and physicists, namely, the possibility of a partial transformation of aragonite into calcite.

There has been quite a number of researches on the formation of calcium carbonate and its modifications, but the results are not yet conclusive. Several authors, however, believe that aragonite is a metastable modification of calcium carbonate. Above 450° only calcite

can exist as a stable modification, but H. W. Foote thinks that the transformation of aragonite into calcite can occur at much lower temperatures, and even at ordinary temperature and pressure. Certainly in that case the time factor must be taken into consideration. This idea finds support among many others, including G. Linck<sup>1</sup> and H. Leitmeier. The latter writer expresses this as follows :

‘Nur unter gewissen Bedingungen wird sich Aragonit bilden können, und nicht nur die Beschränkung durch das Vorhandensein gewisser Lösungsgenossen und durch die Abhängigkeit von der Temperatur macht den Aragonit selten, er stellt ja eine metastabile Phase dar, und wenn auch die Umwandlungsgeschwindigkeit eine ungemein geringe ist, so wird doch im Laufe der Jahrhunderte und Jahrtausende diese Umwandlung der rhombischen in die rhomboedrische stabile Phase eintreten, wie uns ja auch die häufigen Pseudomorphosen des Calcits nach Aragonit beweisen.’<sup>2</sup>

It is quite probable that every crystal of aragonite is subject to a slow transformation into calcite. This can be seen to be probable from the variable specific gravity of aragonite. Calculated from the volume of the unit cell as compared with that of calcite (sp. gr. 2.715), the theoretical specific gravity of aragonite is 2.948; but the actual specimens show a great deviation in many cases. H. Leitmeier gives eleven analyses of aragonite, the specific gravity of the specimens varying from 2.84 to 3.13. The author has determined the specific gravity of several specimens at his disposal. The average specific gravity of six specimens of Bilin aragonite is 2.922; the average sp. gr. of four pyramidal aragonite crystals from Cumberland is 2.904. The higher specific gravity can always be explained by the presence of strontium and lead carbonates, but there are (in Doelter) several specimens the sp. gr. of which is lower than the theoretical, in spite of the fact that there is an admixture of heavier carbonates. This can only be explained on the assumption that aragonite has undergone a partial transformation into calcite.

The mechanism of this transformation will be the subject of another paper, but it may be mentioned here that the first stage of this transformation consists in bringing all the oxygen atoms in the horizontal planes containing the carbon atoms so as to form the  $O_3$  triad group. Only one third of all oxygen atoms, namely  $O_a$ , partake in this translation. One half of them move upwards through a distance  $d_{c/2}$ , the other half

<sup>1</sup> G. Linck, Über die Bildung der Carbonate des Calciums, Magnesiums und Eisens. C. Doelter's Handbuch der Mineralchemie, 1911, vol. 1, p. 113.

<sup>2</sup> H. Leitmeier. Ibid., 1912, vol. 1, pp. 350-1.

moving an equal distance in the opposite direction (fig. 4). As seen on the diagram this movement of oxygen atoms will produce a doubling of spacing for the plane (102). Carbon atoms are also forced to move a very small distance during this first stage of transformation, and this probably produces the doubling of (011) spacing.

If the hypothesis outlined above can be accepted, then all the spacings calculated are in a perfect agreement with spacings observed, and the leptonic model for aragonite finds its justification in the X-ray study.

The question of the intensities of X-ray spectra is much too complex and the knowledge of it is still too imperfect, and therefore we cannot take it into consideration in this paper. But a general comparison between the structures of

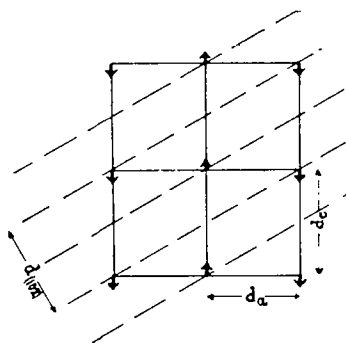


FIG. 4. Schematic projection of the oxygen lattice on a plane perpendicular to (102).

some faces and the observed spectra can be made. The spectra of faces (100), (102), and (130) can be grouped together (in Table II) as they all show the same characteristic decrease of intensity with the order. The structures of (100) and (102) are absolutely identical, but the structure of (130) is slightly different, the carbon atom being here detached from the  $\text{CaCO}$  group. The spectrum of this face in comparison with the first two spectra shows a reduction of the first-order intensity and may serve as a bridge towards the next group where the first order is completely absent. This group of spectra consists of (010), (110), and (011). In the case of the first two faces of this group there is a striking analogy between their structures and their spectra. The structure of (011) is different and its spectrum is different in having the third as well as the first order absent. This, also, may suggest a possible explanation of the double spacing for the face (011), if we remember that every translation of particles may greatly influence the intensity, and the face under consideration is one which could be affected by the transformational movements of carbon atoms.

Before leaving the subject of leptonic structure, there is another interesting matter to be noticed. Fig. 5 represents the reticular densities ( $\delta$ ) of planes plotted against the corresponding spacings ( $d$ ). In general, by reticular density we understand the number of points per unit area, but as in the case of polyatomic compounds the points (atoms) are not equivalent, we have therefore taken into consideration their atomic numbers. The reticular density in our case is calculated by

dividing the atomic number of the  $\text{CaCO}_3$  molecule ( $N$ ) by the area which it occupies in a given plane.

$$\text{Reticular density} - \delta = \frac{N}{\text{Ret. Area}}$$

The equation  $d = f(\delta)$  is represented on the diagram as a straight line, and therefore it can be expressed as  $d = k \cdot \delta$ , where  $k$  is constant, namely  $\tan \alpha = 1.122$ .

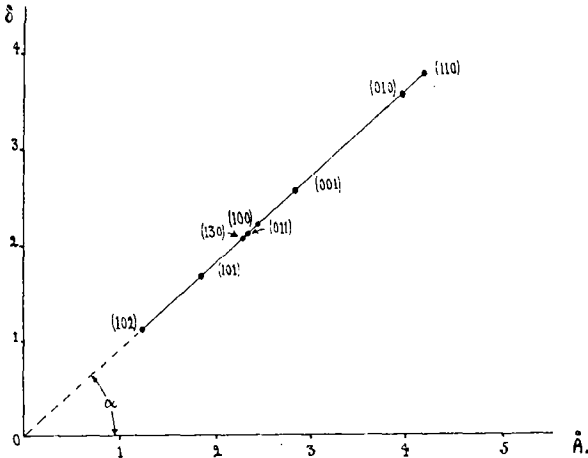


FIG. 5. Reticular density ( $\delta$ ) plotted against spacing ( $d$ ) for several planes in aragonite.

This figure can also be derived in a different way. In the case of face (001) we have

$$\delta = \frac{N}{2d_a d_b} \quad \text{therefore} \quad d_c = \frac{N}{2d_a d_b} k$$

$$\text{and} \quad k = \frac{2d_a d_b d_c}{N} = \frac{56.04}{50} = 1.122.$$

From these equations we can also find that  $2Nk = 112.2$ .

The volume of unit cell is  $112.18 \text{ \AA}^3$  (p. 414), and therefore :  $2Nk =$  volume of unit cell in  $\text{\AA}^3$ .

It is quite clear that the equation  $d = k \cdot \delta$  is an expression of Mallard's law on the relationship between the reticular densities of faces and their distances from the centre of symmetry. It is of some interest to notice that from the same diagram we find the confirmation of the law of Bravais-Mallard, stated as follows :

'Il faut choisir le réseau cristallin de telle sorte que si l'on range les divers

plans réticulaires de ce réseau suivant l'ordre croissant des densités réticulaires cet ordre représente l'ordre croissant des facultés de production, soit matérielle (par la cristallisation), soit artificielle (par le clivage) des faces cristallines correspondantes.<sup>1</sup>

In other words, the law means that cleavage-planes, as well as faces most frequently occurring on the crystal, are those which have the highest reticular density. Fig. 5 shows that faces (110) and (010) have the highest reticular density. These two faces, besides being the most important faces on a crystal of aragonite, also are cleavage-planes. This shows that the law of Bravais-Mallard has its perfect justification in the proposed structure of aragonite.

*Study by means of Etch-figures.*

The etch-figures are considered to be one of the most important factors for the determination of the hidden symmetry of crystals. The leptonic structure of aragonite suggested above possesses only two elements of symmetry of the first kind, and this would place it outside the orthorhombic system. This was the consideration which led the author to try the method of etch-figures. As we shall see later on, the etch-figures on aragonite do not show all the elements of symmetry present in the leptonic structure (no axis of symmetry can be derived from the etch-figures). On the other hand, the etch-figures do not show any additional elements of symmetry, and therefore this method of investigation led to the same conclusion that the symmetry of aragonite is lower than the orthorhombic. This fact taken alone is of a great value, but the etch-figures have been found to be of a much greater importance, since, as it will be shown eventually, they can be used for the determination of the leptonic structure itself, and not merely of its symmetry.

The etch-figures, which are minute pits with polyhedral surfaces, are produced by a rapidly-acting solvent applied for a short time on a crystal-face. The process of solution, as one would expect in an anisotropic structure, does not act uniformly in all directions, but has a directional (vectorial) magnitude. In a sense, this process can be considered as the reverse of crystal-growth, which is a typical vectorial property. It is quite obvious that the most stable planes on a crystal are the planes of the greatest reticular density, which are also the planes of the most frequently occurring faces. The solvent probably begins to

<sup>1</sup> E. Mallard, *Traité de cristallographie*, 1879, vol. I, p. 306 (incorrectly numbered 305).

act in certain detached spots on the surface of the face where the natural resistance is somehow weakened (fractures, scratches, &c.). Starting at a point, the solvent would by itself tend to produce a hemispherical hollow. The action of the solvent may be compared to the work of a miner. A homogeneous material, like clay, will allow the production of a perfectly hemispherical hollow, but if the material possesses natural planes of cleavage, the surface of the hollow, instead of being smooth, will be angular and bounded by pre-existing planes. So in crystals we have a heterogeneity of structure, and the action of the solvent is counteracted by the molar anisotropic resistance of the particular grouping of atoms. The most easily detachable atoms are removed first, leaving planes of greatest resistance—the facets of the *etch-figure*.

The shape of the *etch-figure* is determined by three principal factors :

- (1) The nature of the solvent and its temperature.
- (2) The time during which the solvent is acting.
- (3) The leptonic structure of the crystal.

Taking the first two factors as constant, we can reduce the variables to one, namely, the structural factor.

After testing several solvents, it was decided that hydrochloric acid gives the best results. The acid used was fairly strong (50–70 %), and the time of action was short. The individual exposure varied from one to five seconds, but as different faces were differently affected by the etching medium, repeated etching had to be used in most cases. The etching was carried out at room temperature.

The yellowish crystals of aragonite from Bilin were used for the *etching of the principal faces of the prismatic zone*. Also two artificial faces (100) and (001) were prepared and etched with fairly good results. Some acute pyramidal crystals from Cumberland were also tried, but without any success, the *etch-figures* produced being too small and numerous. The crystals of the Hancock collection exhibited on all the principal faces some natural *etch-figures*. Although a number of these figures were of macroscopical size, they were of little use (except on the face (110)) for our purpose. The natural *etch-figures* were usually rectangular or triangular pits with corroded interior and often filled with yellowish material. Some of the faces of one or two crystals were carefully etched with acid, so as not to spoil their general appearance.

A very interesting observation was made on the process of development of the *etch-figures* during continuous etching. In all cases, the first figure produced was of the simplest type, consisting of three or four

facets forming an inverted pyramid. On further etching, the figure not only grew in size, but also in complexity. New facets were added in a certain regular fashion, either by the replacement of the original facet by a pair of related facets, or by truncation or bevelment of an edge between two facets. A typical development of facets is illustrated on fig. 7, where three successive forms of facets on the face (010) are drawn diagrammatically. One can clearly see that the gradual replacement of the primitive facet by a number of secondary facets may lead ultimately to the production of a curved facet. The curvature of facets after repeated etching can probably be explained by this process of replacement (see photo. no. 1, plate VI). The last stage of etching is reached with a production of circular or elliptical pits with concave sides, in which sometimes some traces of the original facets are preserved (see photo. no. 3).

Another observation was that, on some faces, figures were developed which are mirror reflections of one another. They could not be called enantiomorphous, in the strict meaning of that term, as they can be brought into a congruent position by a rotation around a digonal axis normal to the face. The term *metastrophic*<sup>1</sup> perhaps would be more suitable for them. Such *metastrophic* figures occur in a haphazard fashion on the surface of a given face, and are not, as one might suppose them to be, produced in consequence of the presence of some vicinal faces replacing the face under observation. *Metastrophic* figures were observed on the following faces: (010), (100), and (001).

The etch-figures of seven faces of aragonite were carefully studied and compared with the reticular structure of corresponding faces as shown by the leptonic structure here described. A simplified diagrammatic representation of the etch-figures observed, together with those deduced from the structure, is given on figs. 7, 8, and 9. In all cases the atoms (without any distinction of kind) of the first layer are represented by blank circles, the atoms of the second by crossed circles, and the atoms of the third by black circles.

There is only one plane of symmetry (100) shown by the etch-figures. The digonal axis present in the leptonic structure is not shown by them. The symmetry complex derived from the etch-figures is, therefore, lower than the complex derived from the leptonic structure. If the proposed leptonic structure is a true one, then the etch-figure method of symmetry determination is not quite valid, at least in its application to aragonite.

Before proceeding with the detailed analysis of etch-figures, it would be

<sup>1</sup> N. Story-Maskelyne, *The morphology of crystals*, 1895, p. 99.

as well to discuss the problem for a simple theoretical case. Let us take, for example, a body-centred cubic lattice. The projection on the cube-face of this lattice, as well as the section normal to it, are given on fig. 6. Removing the five central atoms, we leave a depression in the form of a regular quadrangular pyramid. The pyramidal faces of this figure are produced by planes passing through parallel rows of points lying in the odd and even layers respectively. The facets produced have rational indices of the simplest kind, i. e. (110), (101). We may suppose that this will be the shape of a simple etch-figure. As a matter of fact

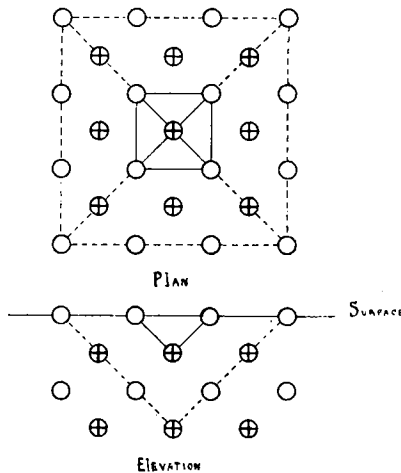


FIG. 6. Plan and elevation of a body-centred cubic lattice, to illustrate the theoretical production of etch-figures.

we can observe similar etch-figures on some cubic crystals (though probably with faces of higher indices).

Let us now apply this method to the actual etch-figures of aragonite. In all cases where this is possible we are going to construct similar figures by passing planes through parallel point-rows situated in the first two or three layers of the given face, so that the intersecting planes would form a closed polyhedral figure.

*Face (100).*—Fairly large, but not too distinct, figures were produced by repeated etching of an artificially prepared face (100). The figures produced are distinctly metastrophic. They have the form of a shallow triangular pyramid, the apex of which in highly developed figures is replaced by a set of secondary facets (*b*, fig. 7). With some difficulty



the facets were examined under a microscope (high-power lens) and the angles (on the (100) projection) measured with a certain degree of approximation. The interfacial angle between (100) and the largest

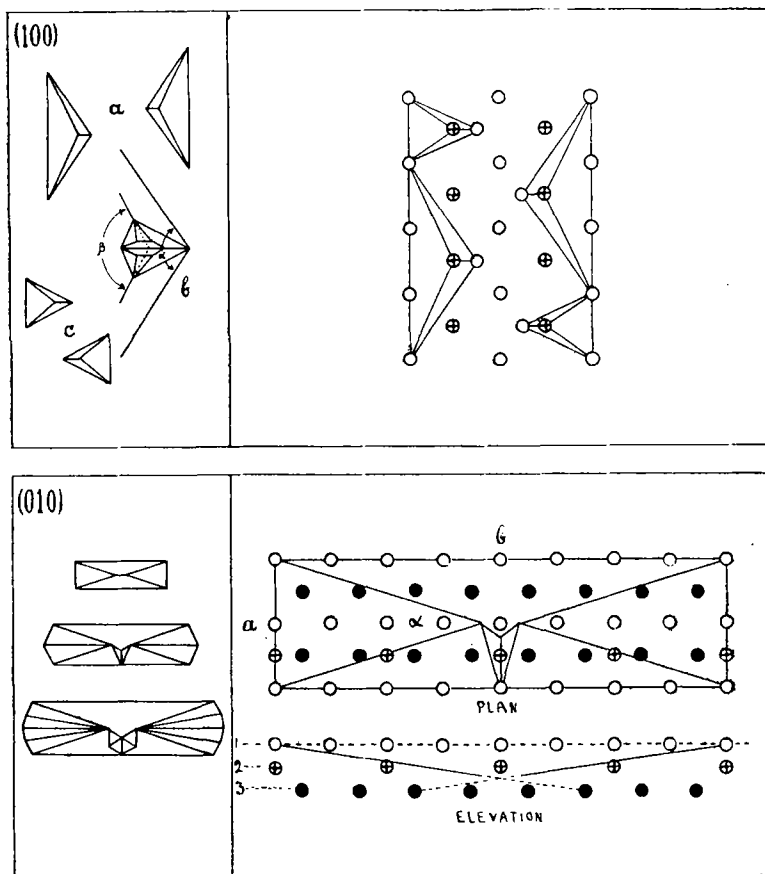


FIG. 7. Diagrammatic representation of the observed (left side) and deduced (right side) etch-figures of aragonite. (Blank circles represent atoms in the first layer, crossed circles those in the second layer, and black circles those in the third layer downwards.)

triangular pyramidal facet has been measured by combining the Miers reflecting goniometer with the microscope. The signal slit used was necessarily a large one, with the result that the angle found varied between certain limits. The results of measurements are presented in

Table III (p. 428), and the corresponding etch-figure on fig. 7 (left side).

Fig. 7 (right side) gives the projection of two first layers of the face (100) of the leptonic model proposed. The simplest figure to be derived by using our method is a small triangular pyramid (*c*, fig. 7). This pyramid has a base which is nearly an equilateral triangle. Similar etch-figures were actually observed, but they were few in number and not distinct enough to be measured. Another figure that can be derived is an elongated pyramid, in all respects analogous to the actual etch-figure (*a*, fig. 7). As one can see, two similar, but metastrophic, figures can be derived from the reticular structure of the face. This similarity extends only to the similarity of projections. The pyramid actually drawn is very deep, and the indices of its facets are (110), (121), and (121) respectively. This does not correspond to the actual figure. But if we take a larger analogous (not similar) figure, we get a very close correspondence between the figure calculated and the actual etch-figure. This is evident from Table III, where the angles calculated are placed alongside the values for the same angles derived from the actual measurements. Taking into consideration the irregularities of the etch-figures and the necessarily rough nature of the methods used for the determination of angles, the agreement between the values is quite close. The indices of the pyramidal facets on the deduced figure are (510), (521), and (521).

*Face (010).*—This face is etched quite easily, and the figures produced are usually quite clear and well defined. The primitive figures are symmetrical domatic pyramids, but, on further etching, some facets are added on one side, producing an asymmetry with regard to the (001) plane. The development of etch-figures is shown diagrammatically in fig. 7. The figures are metastrophic (Plate VI, fig. 1). The principal angles and dimensions were measured by the same method as used in the case of face (100) and the results are shown in Table III.

A figure similar to the etch-figure can be constructed on the face of the leptonic model, but this construction is much more complicated than it was in the previous case. Three successive atomic layers have to be taken into consideration. The first and the third layers determine the principal facets, probably because they are the densest layers. The second layer, with asymmetrically distributed points, determines the small asymmetrical secondary facets. We may suppose that the primitive facets are always formed by particles lying in the densest layers, and that other layers come into play on further etching. Fig. 7 (right side)

gives a projection of the first three layers of the face (010). In view of economy of space the planes are made to intersect between the atomic layers, but this can be avoided by constructing a similar figure on a larger scale (involving more points). All facets have rational indices. There is a good agreement between the values of angles in both the observed and deduced figures (Table III), and we are quite justified in considering the constructed figure as representing the actual etch-figure.

*Face (110).*—The etch-figures developed on this face are particularly interesting, as they show a striking contrast between the natural and artificial etching. The natural etch-figures visible to the unaided eye are well developed on many (110) faces of crystals from the Hancock collection. The facets are corroded but well defined (Plate V, fig. 2). The general shape of the natural etch-figures is of a triangular asymmetrical pyramid, pointing towards the face (010). In the majority of cases the edges are truncated or bevelled. The resulting figure resembles in some respects a deformed primitive figure of the face (010). The etch-figures produced by the action of acid are in the majority of cases almost regular triangular pyramids pointing towards the face (100), i.e. in the opposite direction to the natural etch-figures (Plate VI, fig. 2).

Applying our method, we can easily construct on the leptonic model of the given face, a figure similar to the etch-figure produced by acid. This is done by joining three points of the first layer with one point of the second layer. We get then an almost regular triangular pyramid (fig. 8). It was found to be quite impossible to reproduce the natural etch-figure using the first two layers alone, but taking into consideration the first three layers, a figure closely resembling the natural etch-figure can be reproduced (fig. 8). The interfacial angle of this natural etch-figure could not be measured, but the general proportions correspond very closely to those of the constructed figure.

*Face (011).*—The etch-figures are very small and the measurement somewhat difficult. But every figure produced is well defined. It has the shape of a quadrangular pyramid with the apex shifted towards the face (001). In the later stages of etching the pyramidal edges become truncated (fig. 8).

The figures constructed on the projection of the leptonic structure of the face (011) are of two possible types: (1) triangular pyramid and (2) quadrangular pyramid. The first of the two has been very vaguely observed among the first, almost sub-microscopic, crop of etch-figures; the second obviously corresponds to the observed figure (fig. 8). The values calculated and observed are given in Table III. It was impossible to measure

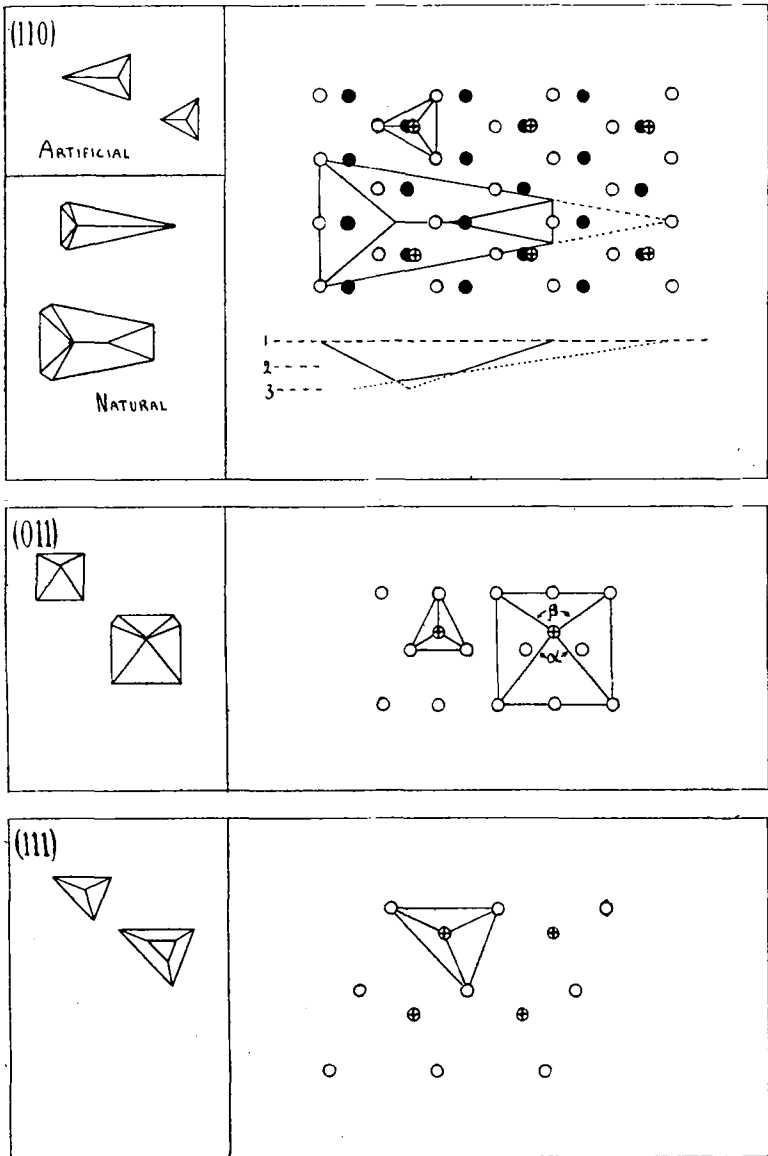


FIG. 8. Etch-figures on aragonite (cf. fig. 7).

the angles very accurately or to determine the interfacial angle, but the general similarity is very good. The indices of the constructed figure are (021), (023), (144), and ( $\bar{1}$ 44).

TABLE III.

Face.	Angles and ratios.	Observed.	Number of observation.	Calculated.
(100)	(100) : (510)	6° - 7½°	5	7° 9'
	<i>a</i>	110 - 114	5	111
	<i>β</i>	124 - 129	5	130
(010)	(100) : ( $\bar{1}$ 31)	9 - 10	3	9 12
	<i>a</i>	34 - 56	3	34 30
	<i>a</i> : <i>b</i>	0.295	10	0.282
(011)	<i>a</i>	76° - 78°	5	75° 30'
	<i>β</i>	115 - 120	5	112

*Face (111).*—The etch-figures are small triangular pyramids, the apex of which is very often truncated by a face parallel to the base. The sides of the triangular base are parallel to the edges (111) : (001), (111) : (100), and (111) : ( $\bar{1}$ 11), respectively. The constructed figure (fig. 8) is perfectly similar in its general aspect with the actual figure.

*Face (001).*—The etching process goes too rapidly on this face, and the only figures produced were elliptical hollows with a trace of a triangular facet at the bottom. This triangular facet is pointing in opposite directions in different pits (Plate VI, fig. 3), and therefore the figures are metastrophic. The faces were prepared by grinding, and this probably explains the metastrophic nature of the etch-figures.

In fig. 9 we have a construction of two possible figures out of two successive pairs of layers: (*a*) first and second layers, (*b*) third and fourth layers (grinding probably does not follow one atomic layer, and so the alternate layers are exposed on the surface). By successive replacement of facets the polyhedral surface of the etched pit gradually assumed the trough-like shape, while preserving intact the triangular horizontal facet seen in the actual etch-figure.

*Face (1. 16. 0).*—Some unusual faces of the prismatic zone were observed on a large crystal of aragonite from Bilin, Bohemia. The interfacial angle between one of these faces and the (010) face was found to be 5° 50', corresponding with the indices (1. 16. 0) (calculated 5° 48').

The etch-figures produced on this face are extraordinarily good, well shaped, and not too crowded together (Plate VI, fig. 4). They exhibit a very striking feature, which has not been previously observed with any other etch-figures, namely, a marked tendency to form rows parallel to the *c*-axis. The figures appear to be symmetrical with regard to the

horizontal plane, but absolutely asymmetrical in a vertical direction. The orientation is the same for all figures. Four pyramidal facets  $c, c', d, d'$  (fig. 9) make the primitive figure. Further development leads to the appearance of additional facets either truncating the edges or re-

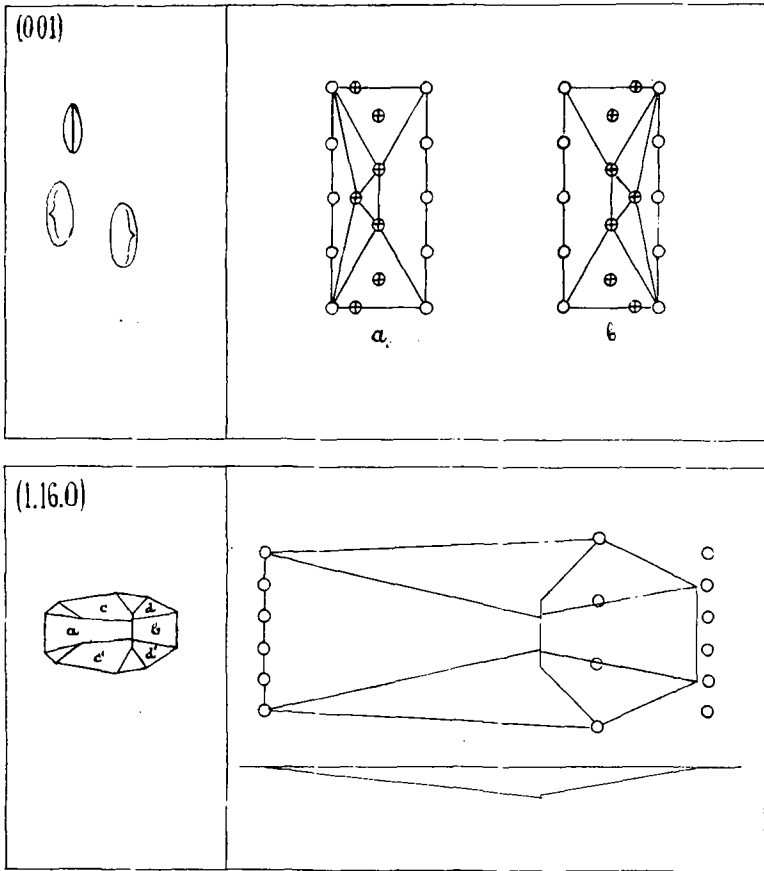


FIG. 9. Etch-figures on aragonite (cf. fig. 7.)

placing the pyramidal facet by a pair of conjugate facets. Every additional etching increases the number of facets until an elliptical pit is produced.

The micro-goniometric measurement gave for the interfacial angle  $a : (1.16.0)$  approximately  $5^{\circ} 50'$ , proving the facet  $a$  to be  $(010)$ . This

facet was present in all etch-figures. It was found impossible to get accurate measurements with the facet  $b$ , and its indices were approximately determined by the measurements of the ratio of its length to the length of facet  $a$  (projection on the plane of the face etched). These measurements showed that while the indices of the facet  $a$  remained constant, the indices of facet  $b$  varied.

From the observation of etch-figures in general, we can draw the conclusion that the principal facets (usually the first formed) are those of the greatest possible reticular density and inclined at a comparatively small angle to the etched face. It is quite possible that the facets subsequently formed follow the law of decreasing reticular density. Our first statement can find its support in the figure in question. Facet  $a$  (010) is certainly a plane of greatest reticular density among all the faces of aragonite. This is why it is so constantly developed in the etch-figure. The second variable facet  $b$  in the prism-zone may be formed by such planes as (110), (120), (130), (140), (150), (160), &c., all with a relatively high reticular density.

The largest and the best-shaped figure was selected as a typical example. This particular etch-figure is represented in fig. 9. The ratio of the length of the facets  $b:a$  was found to be approximately 2. The leptonic structure of the face (1.16.0) was drawn in plan and side elevation (fig. 9), and the theoretical ratios for different values for  $b$  were calculated. They range from 14.5 for face (110) to 2.1 and 1.9 for (150) and (160) respectively. It is thus evident that the facet  $b$  must be either (150) or (160). Plane (160) was chosen because the curvature of the actual facets slightly affects the measurements, and the true ratio is probably less than 2.

From fig. 9 (right) it is seen that the atoms of the (1.16.0) plane are distributed along definite rows parallel to the axis  $c$ . Removing two atoms from the less packed row we can trace the outline of our etch-figure quite easily; and the indices for the constructed figure are  $a$  (010),  $b$  (160),  $c$  (1.16.5),  $c'$  (1.16.5),  $d$  (7.24.3),  $d'$  (7.24.3).

The general agreement between the figures deduced by construction and the figures observed is more or less good. This fact brings another support to the leptonic structure of aragonite constructed in accordance with the X-ray spectra.

Up to the present time, the etch-figures have been used only for the detection of hidden symmetry. This, as shown above, is not an entirely reliable method. But the etch-figures show something more than mere symmetry—they reveal the actual leptonic structure. It would be difficult

at the present time to use the etch-figures for the direct determination of the leptonic structure, but they may become a powerful method of testing the structures already constructed by means of X-ray analysis.

*The Symmetry of Aragonite.*

The leptonic model of aragonite here proposed shows the following elements of symmetry :

$$\begin{array}{l} \text{1st sort} \left\{ \begin{array}{l} \text{Digonal axis . . . . . } a_2. \\ \text{Plane of symmetry . . . . . } (100). \end{array} \right. \\ \text{2nd sort} \left\{ \begin{array}{l} \text{Digonal screw-axis . . . . . } c_2. \\ \text{Glide-plane of symmetry . . . . . } (010). \end{array} \right. \end{array}$$

These operations of symmetry form a finite group of the second sort, which, according to definition,<sup>1</sup> contains as many operations of the first sort as of the second sort. This is the group  $C_2^h$  of monoclinic holohedry. The presence of the elements of symmetry of the second sort is merely due to a certain position of the carbon atoms and is in no way characteristic of the given group. Placed along the vertices of the lattice  $\Gamma_m'$ , this point-group will form the space-group  $C_{2h}^1$  isomorphous with  $C_2^h$ .

But in our case we have a monoclinic point-group placed along an orthorhombic space-lattice. It is well known that every class of crystal-symmetry is defined by the symmetry elements alone, the crystallographic axes being only the axes of reference, and chosen in such a way as to give the simplest representation of faces by mean of indices. We must also remember that the orthorhombic space-lattice is a limiting case of the monoclinic lattice, when the angle  $\beta$  becomes equal to  $90^\circ$ . So we can consider the orthorhombic space-lattice in our case to be  $(\Gamma_m')_{\beta=90^\circ}$ . This particular case, when the lower space-lattice exhibits an approximation to a space-lattice of a higher symmetry, is called a limiting or pseudo-symmetry.

Therefore, we must consider aragonite as a pseudo-orthorhombic crystal of the monoclinic system. This fact has been already suggested long ago by Beckenkamp, Wallerant, and Viola. The explanation of this pseudo-symmetry was sought by the first two authors in twinning, but this was probably due to the attempt to interpret the metastrophic etch-figures. It is obvious that we can dispense altogether with this explanation and look for the pseudo-symmetry in the leptonic structure

<sup>1</sup> H. Hilton, *Mathematical crystallography*, 1903, p. 46.



itself. Our conclusions are much nearer to those of Viola, who expresses his idea as follows:

‘Wir haben nun für den Aragonit dieselbe Erscheinung wie bei anderen polymorphen Substanzen, nämlich, dass die Molekelhaufen die prismatische Symmetrie besitzen, während das Raumgitter dem rhombischen Systeme entspricht . . . Der Aragonit besteht aus einem Aggregat von monoklinen, gleich orientirten Theilchen, die nach einem rhombischen Skelett angeordnet sind.’<sup>1</sup>

It is also well known that aragonite has the tendency to form complex twin intergrowths, in such a way as to produce crystals resembling those of the hexagonal system. The tendency to produce mimetic forms is even far stronger in the case of witherite and cerussite, which are nearly always found in pseudo-hexagonal forms. ‘Now it is one of the most remarkable facts observed in inorganic nature, that such pseudo-symmetrical crystals exhibit a strong and undeniable tendency to increase their deceptive appearance yet more by repeated twinning and regular aggregation.’<sup>2</sup> As a matter of fact, aragonite, being a pseudo-symmetrical crystal, tends to increase its symmetry in two different ways: (1) by means of twinning; (2) by a direct transformation into a rhombohedral crystal of calcite. Both of these ways are probably the direct manifestation of the same tendency.

‘Cette tendance vers la symétrie est une des grandes lois de la nature inorganique . . . Elle n’est d’ailleurs qu’une manifestation de la tendance plus générale de la nature vers la stabilité, c’est-à-dire vers le repos,—tendance, qui est une des grandes forces antagonistes de l’univers.’<sup>3</sup>

#### *The Unit cell of Aragonite.*

As a unit cell of aragonite the rhombic prism  $\{110\}$  closed by  $\{001\}$  was chosen. Its volume is equal to  $112.18 \text{ \AA}^3$ , and it contains two molecules of  $\text{CaCO}_3$ . According to Bragg the definition of the unit cell is as follows: ‘The unit of crystal structure is the smallest portion of a crystal which, repeated through space without change in character or orientation, makes up the crystal.’<sup>4</sup> The unit cell of aragonite as represented in fig. 1 does conform to this definition, and therefore it is taken to be the correct unit cell. The space enclosed by this cell represents one of Fedorov’s parallelehedra (triparallelohedron). A close packing of a number of similar cells will reproduce the orthorhombic space  $\Gamma_0'$ . Each cell can be further subdivided into two identical but differently orientated polyhedra (stereohedra) by passing a diagonal plane parallel to the

<sup>1</sup> C. Viola, Ueber den Aragonit von Sicilien und seine Structur. Zeits. Kryst. Min., 1897, vol. 28, p. 230.

<sup>2</sup> F. M. Jaeger, Lectures on the principle of symmetry, 1917, p. 172.

<sup>3</sup> E. Mallard, 1880. [F. M. Jaeger, loc. cit., p. 166.]

<sup>4</sup> W. H. and W. L. Bragg, X rays and crystal structure, 1924, p. 149.

axis  $a$ . The volume of such a stereohedron will be half of that of the unit cell and it will be associated with one molecule of  $\text{CaCO}_3$ . This space partitioning, as was pointed out by W. Barlow, is 'a mere geometrical fiction',<sup>1</sup> and has no real physical significance, because all atoms forming a crystal are completely interlocked into a gigantic molecule, but it may help us in a better understanding of the symmetry of the crystal.

Replacing the bimolecular group ( $2\text{CaCO}_3$ ) by a corresponding point-group, we can see that every one of such groups is associated with one unit cell. This point-group  $C_2^h$  is derived from the point-group  $C_s$  by the rotation of the latter around a digonal axis. The point-group  $C_s$  corresponds to one molecule of  $\text{CaCO}_3$ , which, multiplied by a digonal axis, will give the point-group  $C_2^h$ .

This representation of the aragonite unit cell seems to satisfy the formula of G. Shearer, who in a recent paper discusses a similar case: 'Thus a molecule with a plane of symmetry may form a crystal of, say, class 5 with only two molecules per cell, the second being derived from the first by a rotation about the digonal axis. This can happen, however, if the plane of symmetry of the molecule is set in the crystal parallel to the plane of symmetry of the crystal.'<sup>2</sup> The formula given by Shearer is  $n/m = p$ , where  $n$  = the symmetry number of the crystal-class (minimum number of asymmetric molecules per unit cell);  $m$  = number of molecules per unit cell;  $p$  = symmetry number of the molecule. In our case we get:  $n/m = 4/2 = 2$ . The symmetry number of the molecule of  $\text{CaCO}_3$  is, therefore, equal to two, and this agrees exactly with the symmetry number of the corresponding point-group ( $C_s$ ). Two of such molecules rotated about the digonal axis normal to the plane of symmetry of the molecule will reproduce the bimolecular group described above.

In giving the representation of the unit cell of aragonite we placed only one bimolecular group within its boundary, leaving some of the vertices of the lattice blank. There is some reason in doing this, although it is not the method usually adopted. In dealing with point-groups we can bring their points in congruent positions, i. e. so that one point on rotation or translation will occupy the position of another point. Such a congruency is impossible to realize when the geometrical points of point-groups are replaced by material atoms. To satisfy the definition of the unit cell as given by Bragg, we had to leave out all atoms with the exception of the minimum number contained in the bimolecular group. A number of cells similar to the one represented in fig. 1 can be packed up so as to fill completely the space, while the whole assemblage will reproduce the leptonic structure of aragonite (minus some of the atoms belonging to the surface layer which have to be added separately). This 'rational' representation of the unit cell, as far as the author knows, has not before been attempted. It may be perhaps more difficult to visualize the whole of the leptonic structure by looking at such a representation, but this can be done by the representation of the 'grosser unit', reserving for the 'unit cell' the representation which would conform to its definition.

<sup>1</sup> W. Barlow, On homogeneous structures and the symmetrical partitioning of them, with application to crystals. *Min. Mag.*, 1896, vol. 11, p. 119.

<sup>2</sup> G. Shearer, Molecular and crystal symmetry. *Proc. Physical Soc. London*, 1923, vol. 35, p. 86.

*Summary.*

Besides an attempt to construct a leptonic model of aragonite, the author presents a new method for the determination of the leptonic structure of crystals from their etch-figures.

The structure of aragonite, constructed in such a way that its transformation into that of calcite can be attained with a small expenditure of energy, was tested by means of the method of etch-figures, and a perfect agreement was reached between the figures observed and those deduced. In case of six faces (out of eight observed) the spacings are in perfect agreement with those observed by W. L. Bragg, the remaining two being half of the observed spacings. This discrepancy is explained by a hypothesis (supported by certain facts) that aragonite in its natural occurrence has undergone a partial transformation into calcite.

The structure proposed is unable to explain the intensities of the X-ray spectra. As the knowledge of intensities of X-ray spectra is still very imperfect, this question is not discussed; but it is possible that the cause of this discrepancy may be also sought in the partial transformation of aragonite into calcite.

The constructed leptonic model of aragonite belongs to the space-group  $C_{2h}^1$ , and, therefore, this mineral is monoclinic, and not orthorhombic, as previously thought. This fact, already remarked upon by some mineralogists, places aragonite in the holohedral class of monoclinic system. But as its crystallographic axes are orthorhombic, the monoclinic crystals of aragonite are considered to be pseudo-orthorhombic.

## EXPLANATION OF PLATE VI.

Photomicrographs of etch-figures on aragonite (from Bilin, Bohemia).

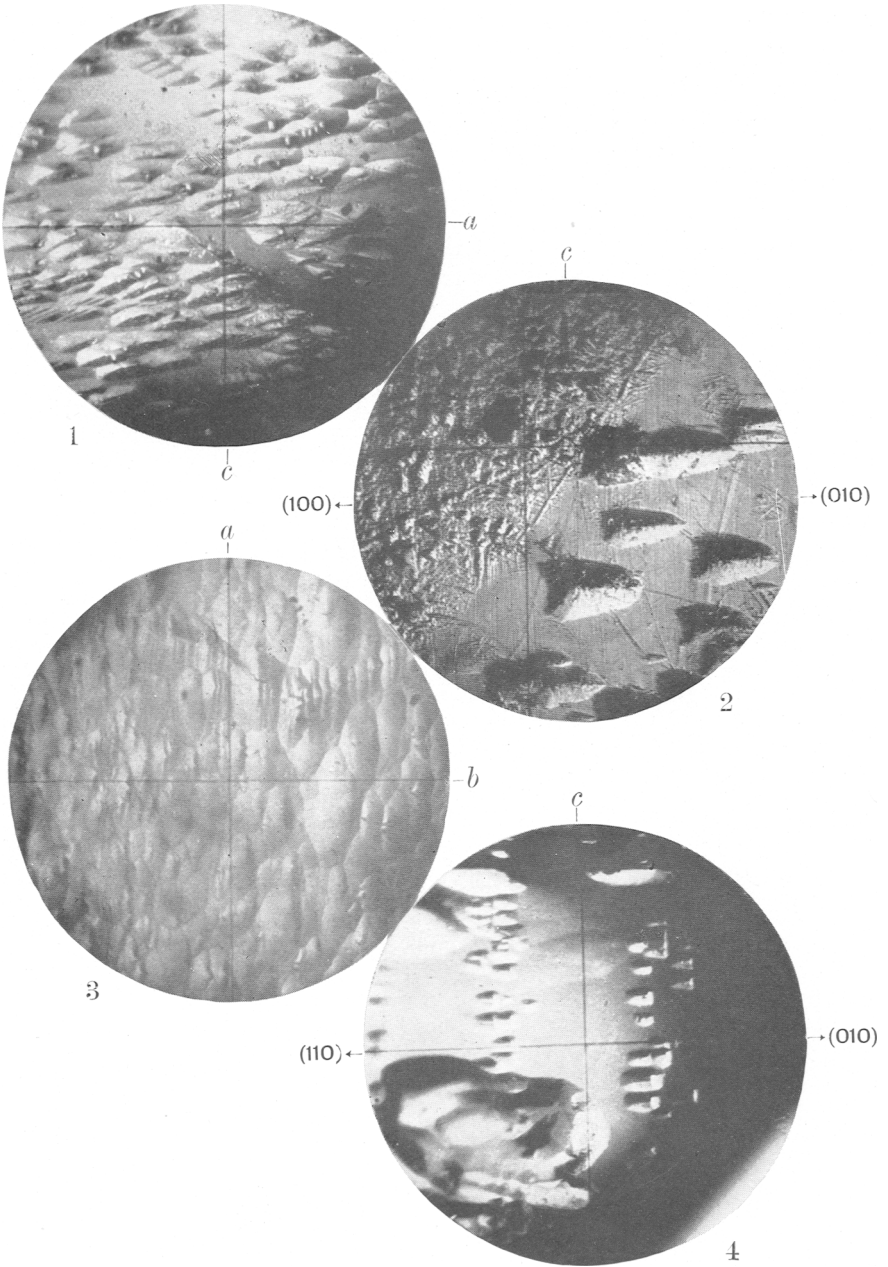
Magnification  $\times 35$ .

FIG. 1. On the face (010). Metastrophic etch-figures, produced by hydrochloric acid.

FIG. 2. On the face (110). Natural etch-figures on the lower right-hand side; artificial figures produced by hydrochloric acid on the upper left-hand side.

FIG. 3. On an artificial face ground approximately parallel to (001). Metastrophic etch-figures, produced by acid.

FIG. 4. On the vicinal face (1.16.0). Etch-figures produced by acid.



S. TOMKEIEFF: ETCH-FIGURES ON ARAGONITE.