BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 39 2361—2364 (1966)

The Superstructure in Fine Aragonite Particles

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(Received April 9, 1966)

An electron diffraction study was done with fine aragonite particles about 0.5 to 1.0 μ in size. The specimens were obtained by mixing a boiled calcium chloride solution (0.1 N) with 0.1 N of an ammonium carbonate solution. Extra spots were observed with half-integer indices $\{1/2, 1/2, l\}$. This suggests the existence of a structure that differs from that of normal aragonite. From an X-ray diffraction study of the specimen, a $\{1/2, 3/2, 0\}$ diffraction was also observed. The structure for explaining these half-integer diffractions is presented as a superstructure of aragonite; it belongs to the space group of D_{2h}^{15}-*Pbca*, with cell dimensions of $A=8.420$ Å, $B=9.385$ Å, and $C=5.741$ Å, and it containes 8 formula units in a unit cell. A dark-image photograph shows this anomalous area to be comparatively wide and suggests that the anomalous area is dominant in a crystal. The authors conclude that rapidly-precipitated aragonite powders contain a small quantity of the repeatedly-twinned crystals mentioned above.

There are, as is well known, three modifications of calcium carbonate; calcite with a rhombohedral structure, aragonite with an orthorhombic structure, and vaterite with a hexagonal structure. Furthermore, many investigations of polymorphism in calcite have revealed the existence of calcite I, II and III,¹⁾ which differ from each other only in the orientation of their carbonate groups.²,³⁾

However, no such anomalous structure has yet been reported for aragonite except for the twin structure proposed by Bragg.⁴⁾ This twin structure is made up of two crystals intersecting on the (110) plane, arrangements of the cabonate group being symmetrical with this plane.

In the course of a study of the phase transformation of aragonite to calcite,* the present authors

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1) P. W. Bridgeman, *Am. Jour. Sci.*, **237**, 7 (1939).
2) J. J. Lander, *J. Chem. Phys.*, **17**, 892 (1949).
3) J. C. Jamieson, *J. Geol.*, **65**, 334 (1949).
4) W. L. Bragg, *Proc. Roy. Soc.*, **A-105**, 16 (1924).
* Y. Hiragi, N. Nakanishi, T. Takada and S. Kachi, to be published.

found a new structure of aragonite. The electron diffraction patterns taken from fine crystals of aragonite exhibited extra spots involving half-integer indices which cannot be explained by the ordinary structures. As a result of the analysis, the new structure was found to correspond to a superstructure with regard to the orientation of the carbonate ion group.

Experimental

To obtain fine particles of aragonite suitable for electron diffraction, the following procedure was carried out: Equal volumes of solutions of calcium chloride (0.1 N) and of ammonium carbonate (1.0 N) were prepared; then both were boiled to 100°C and mixed together to precipitate calcium carbonate. The precipitate was soon filtrated and dried. Although it is difficult to obtain pure and fine aragonite powders, almost 100 percent of the aragonite was precipitated under these conditions. The water suspension of the particles was dispersed by ultrasonic waves to obtain pieces of aragonite crystals, which were a few μ long and a few thousands of Å wide and thick.

They were examined by the direct transmission of a selected area in an electron microscope with an applied voltage of 50 kV. It generally happens that the thickness of the particles is so large that the electron beam can not easily penetrate the particles. However, one can get the diffraction pattern by searching out a thin plate. The X-ray diffraction study was also made by the Debye-Scherrer method, using a diffractometer.

Results and Discussion

Figure 1 (a) and (b) show an electron micrograph and a diffraction pattern taken from aragonite involving half-integer indices. The net diffraction pattern shows that the particle is a single crystal and that it has an orthorhombic lattice. Figure 2 shows the indices of the diffraction pattern, based on the normal aragonite lattice. The results of the analysis are shown in Table I, in which the $d_{calc.}$ values were calculated from the cell dimensions given on the A. S. T. M. card 5—0453. Figure 3 (a) and (b) show an electron micrograph and dark-image photographs of a fine aragonite particle. Figure 4 shows a part of the X-ray diffraction chart of the aragonite powder; the (1/2, 3/2, 0) diffraction was observed as well as the diffraction from normal aragonite.

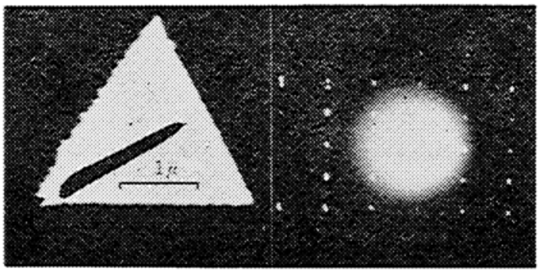

Fig. 1. Electron micrograph and diffraction pattern of super structure of aragonite fine particle.

TABLE I. THE INDEXING OF THE DIFFRACTED SPOTS BASED ON THE LATTICE OF NORMAL ARAGONITE AND THE INTERPLANAR SPACINGS COMPARED WITH THE CALCULATED VALUES

{*h*, *k*, *l*}	$d_{obs.}$	$d_{calc.}$
1/2, 1/2, 0	8.45	8.420
0, 0, 1	5.95	5.741
1/2, 1/2, 1	4.84	4.744
1, 1, 0	4.26	4.210
1, 1, 1	3.44	3.395
0, 0, 2	2.93	2.871
3/2, 3/2, 0	2.85	2.804
1/2, 1/2, 2	2.78	2.714
3/2, 3/2, 1	2.55	2.521
1, 1, 2	2.43	2.372
2, 2, 0	2.12	2.105
3/2, 3/2, 2	2.05	1.965
2, 2, 1	1.99	1.976
0, 0, 3	1.97	1.914
1/2, 1/2, 3	1.91	1.792
1, 1, 3	1.78	1.742

In the case of electron diffraction, the planes which satisfy the diffraction conditions are parallel to the incident electron beam. Hence, it necessarily follows from the analysis of the pattern that the plate of aragonite must have been oriented to the (001) and (110) planes parallel to the direction of the electron beam; judging from the dark image photographs, the [001]axis is parallel to the length of the plate.

The half-integer indices on the electron diffraction and X-ray diffraction patterns cannot be accounted for by a normal aragonite structure. The normal aragonite structure belongs to the space group D^{16}_{2h}-*Pmcn*,4) for which the following conditions limit the possible reflections: for *hkl*: no condition; *hko* : $h+k=2n$, and for *hol* : $l=2n$. Nevertheless, in the present electron diffraction pattern, there appear several forbidden spots which do not satisfy the rule; for example, $(00\bar{3})$, $(00\bar{1})$, (001)...; spots which are denoted by in Fig. 2 cannot satisfy the rule. This observation indicates that the double diffraction occurs in a fairly thick crystal, because generally the electron beam strongly interacts with materials. However, the half-integer indices, whose spots are denoted by ⊠, cannot be accounted for by the normal structure of aragonite, even if the double diffraction effect is taken into account. The half-integer spots can be seen along the [110] axis of the reciprocal lattice shown in Fig. 2. Therefore, the periodicity of the (110) plane must be twice as large as that of normal aragonite; i. e., reflections with {1/2, 1/2, *l*} indices suggest a superstructure which has a repeating unit twice as large as that of normal aragonite. In view of the fact that the *l* indices still remain integers in both electron and X-ray diffraction

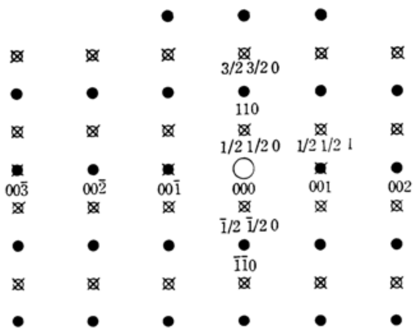

Fig. 2. Indexing of diffraction pattern of Fig. 1.
● Diffraction spots of normal aragonite.
✱ Double diffraction spots of normal aragonite.
☒ Double diffraction spots of superstructure.

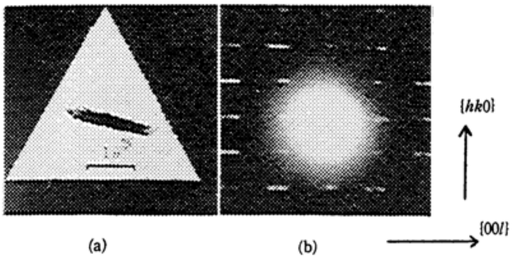

Fig. 3. Electron micrograph and dark image photographs of superstructure of aragonite fine particle.

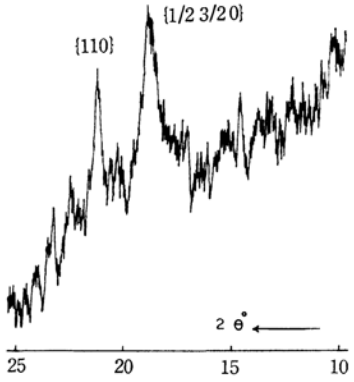

Fig. 4. X-ray diffraction chart, with CuKα radiation, of aragonite fine particles including superstructure of aragonite.

patterns, it must be added that there is no anomaly in the direction of the 'c' axis.

The model for such a structure is presented in the form of the (001) projection in Fig. 5, where only one-half of the structure along the 'c' axis is drawn. The superstructure is constructed so as to repeat the twinning every two layers of carbonate ions on (110) planes; this is called polysynthetic twinning by mineralogists. In Fig. 5, solid lines show the two unit cells of the repeated twinning

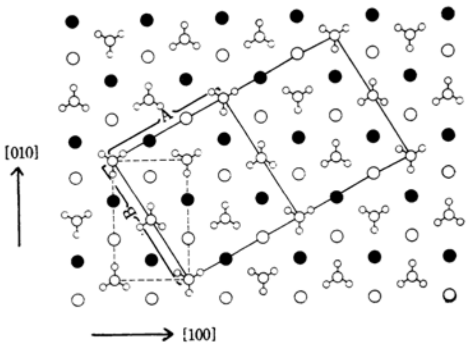

Fig. 5. The (0 0 1) plane projection of the model for superstructure, in which is drawn the position of atoms from 0 to $c/2$. The rigid lines show the unit cells of the superstructure, and broken lines a unit cell of normal aragonite. There is no longer the periodical structure within the broken lines.

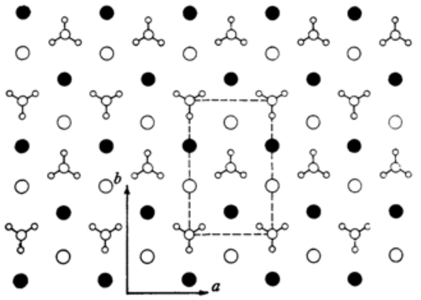

Fig. 6. The structure of normal aragonite projected on (0 0 1) plane.

structure, while the broken lines show a unit cell of normal aragonite. We can see that a periodic structure is lacking within the lines.

For comparison, Fig. 6 shows a (001) projection of the normal aragonite. As can be seen, all CO_3 groups which lie in a row parallel to the 'a' axis are similarly oriented, whereas groups which lie in a row parallel to the (110) plane point alternate ways. Meanwhile, in the superstructure, as Fig. 5 shows, every two CO_3 groups in the row parallel to the 'a' axis of normal aragonite orient in alternate ways, and the groups which lie in a row parallel to the (110) plane of normal aragonite similarly orient in alternate ways, like the case of normal aragonite.

This model is still aragonite, for it has the same layer structure as normal aragonite. It belongs to the space group of D_{2h}^{15}-*Pbca*, with cell dimensions of $A=8.420$, $B=9.385$ and $C=5.741$, and it containes 8 formula units in a unit cell. The relation of normal aragonite to the twinned structure is given by:

$$\boldsymbol{A} = \mathbf{a} - \mathbf{b} \qquad H = h - k$$

$$\boldsymbol{B} = \frac{3}{2}\mathbf{a} + \frac{1}{2}\mathbf{b} \quad K = \frac{3}{2}h + \frac{1}{2}k$$

$$\boldsymbol{C} = \mathbf{c} \qquad\qquad L = l$$

where $\boldsymbol{A}$, $\boldsymbol{B}$, $\boldsymbol{C}$, and H, K, L are, respectively, the unit lattice vector and the Miller indices of the superstructure, and where $\mathbf{a}$, $\mathbf{b}$, $\mathbf{c}$ and h, k, l are those of the normal aragonite.

The content of twinned particles is so small compared to the normal aragonite that the diffraction from the twinned structure is very weak in X-ray diffraction studies. Hence, it is necessary to distinguish carefully the diffracted peaks from the backgrounds. In the present experiments both Fe$K\alpha$ and Cu$K\alpha$ radiations were used to take X-ray diffraction patterns. In the pattern of the diffraction with Cu$K\alpha$ radiation shown in Fig. 4, the (1/2, 3/2, 0) diffraction was observed. It must also be added that this peak is also observed in diffractometry using Fe$K\alpha$ radiation. These findings support the theory of the presence of a superstructure and the appropriateness of the model.

The dark-image photographs show that the area of the superstructure is comparatively large; however, it is still not clear whether or not this area covers all the crystal, for it is generally difficult to get a clear dark-image photograph. Nevertheless, as the superstructure region requires a different structure, one may call this another phase, i. e., aragonite II.

The authors are grateful to Dr. Tsuneo Seto of Tokyo Metropolitan University for determining the space group, and to Prof. Hatsujiro Hashimoto of Kyoto Technical University and Dr. Takeo Ueda of our university for their helpful suggestions. They are also grateful to Dr. Yasumasa Goto and Mr. Koji Kosuge of our laboratory for their fruitful discussions. One of them (Y. H.) wishes to express his gratitude to Mr. Shigeki Shimidzu of the Toda Industry Co., Ltd., and Mr. Shigeo Horii of the Reikoo Co., Ltd., for their support during the work.