# THE CRYSTAL FORM OF BOLEITE*

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Boleite, the composition of which is essentially $PbCl_2 \cdot CuO_2H_2$, with a considerable content of AgCl, is a mineral whose crystallographic character is not well understood. According to the external appearance of the crystals, they belong to the cubic system, commonly occurring as the form (100), or as a combination of (100) and (111). However, according to the investigation of G. Friedel,[1] they should be interpreted as intergrowths of tetragonal crystals. But their cubic habit is not in harmony with the axial ratio $a:c = 1:3.996$; such a large value for the $c$ axis usually being found only in crystals with a pronounced foliated development.

Accordingly this study of the crystal form of boleite was undertaken. Dr. F. Mussgnug, at my suggestion, has determined the lattice constants by means of X-ray methods. Films of very good quality gave the following results:

| Direction | Distance in Ångstrom Units | | |
|---|---|---|---|
| | Observed | | Calculated |
| [100] Cube edge | 15.78<br>15.63<br>15.69<br>15.41<br>15.45 | average 15.6 | — |
| [110] Face diagonal | 22.12<br>22.00<br>21.84<br>21.80<br>21.85 | average 21.9 | $22.06 = a\sqrt{2}$ |
| [111] Body diagonal | 26.78<br>26.72<br>26.85<br>26.85<br>26.80 | average 26.8 | $27.0 = a\sqrt{3}$ |

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[1] *Bull. Soc. Min. Paris*, 1906, **29**, 55.

The values for [100] and [110] were obtained by the oscillation method from a natural (100) face, and that for [111] from an artificial (110) face. The following results were obtained from three films:

| Reflection | Intensity | $\delta$ Calculated | $\delta$ Observed | Remarks |
|---|---|---|---|---|
| 002 | — | 5° 40′ | 5° 40′ | Two films from (100) face with [100] and [110], resp., as axes of rotation. |
| 003 | m. st. | 8° 30′ | 8° 30′ | |
| 004 | v. st. | 11° 22′ | 11° 24′ | |
| 005 | st. | 14° 16′ | 14° 24′ | |
| 006 | st. | 17° 11′ | 17° 24′ | |
| 222 | v. st. | 9° 50′ | 9° 50′ | One film from (111) face, with [101] as rotation axis. |
| 333 | st. | 14° 50′ | 14° 54′ | |
| 444 | m. st. | 19° 57′ | 20° 3′ | |
| 555 | m. | 25° 15′ | 25° 30′ | |

For the calculations, the wave length value was 1.54Å. This value, together with the distance 15.6Å for the cube edge, gave the quadratic formula, $\sin^2\delta = 0.00244(h^2+k^2+l^2)$.

From a comparison of the observed and calculated values, it is evident that the axial ratio cannot be $a:c = 1:3.996$. To be exact, this evidence merely proves that the outer layer of the crystal is cubic. This outer layer must have a considerable thickness, for the values for [111] were determined on a cut face, but nevertheless gave a value of $a\sqrt{3}$. The isotropic nucleus can be seen under the microscope, as is mentioned by Friedel, so it is reasonable to conclude that this portion of the crystal is likewise cubic.

This cubic structure has a unit cube with $a = 15.6$Å. The compound $PbCl_2 \cdot CuO_2H_2$ has the molecular weight $M = 375.8$. The density of boleite is given as 5.054. This would mean that there are 31.2 molecules in the unit cell, if the content of AgCl is ignored. There would be a reduction in the molecular weight, if we assume that there is some isomorphous substitution of AgCl. There would then be satisfactory agreement with the assumption that there are 32 molecules in the unit cell.

Furthermore, there are cube-like crystals, whose outer form can be regarded as right angled interpenetrations of two simple cubes. The outer layer of these crystals are pseudoboleite, according to

G. Friedel. We have determined the spacing for such crystals, including the outer layer, and find that for [100] there is complete agreement with the value $a = 15.6$Å. This outer layer is then indentical with that of the regular boleite. Accordingly, there is doubt as to any difference between the two minerals, and further research should show whether pseudoboleite, with its axial ratio of $a:c = 1:2.023$, really exists.

Under the microscope the structure of the crystals appears rather complex, with both isotropic and anisotropic areas. Such a structure is not revealed at all by the X-ray data. The diagrams show throughout a regular arrangement and, in fact, for the axes of rotation, [100] and [110] they are symmetrical with respect to the zero line. Furthermore, we have obtained a very good Laue diagram from a (100) cleavage, which shows a four-fold axis of symmetry, as well as 2+2 planes of reflection. The films show no evidence not in harmony with the cubic arrangements, possessed by any of the symmetry classes $T_d$, $O$, or $O_h$. From the X-ray data, there is scarcely any other arrangement besides regular cubic possible.

The anisotropic character of portions of the crystals, as revealed by the polarizing microscope, can be considered as due to optical anomalies. The atomic centers of gravity are arranged in a cubic lattice. But the atoms themselves are in a strained condition, perhaps because of the isomorphous replacement, and this strain is the cause of the anomalous optical behavior.

The group boleite-pseudoboleite-cumengite still shows unsolved problems with respect to its chemical and crystallographic properties. There appears to be a possibility of solving these problems by the X-ray method. We plan to extend the chemical and crystallographic study as much as possible and have already begun the investigation of this rather comprehensive problem which embraces a large mass of details.