

SYMMETRY OF PHOSPHOSIDERITE

DUNCAN McCONNELL, *The University of Texas,
Austin, Texas*

INTRODUCTION

Prior to the description of crystals from Sardinia by M. de Angelis (1) in 1926, phosphosiderite was supposed to exhibit the external symmetry of a substance belonging to the orthorhombic holohedral class. This mineral had been investigated by H. Laubmann and H. Steinmetz (2) as well as the authors who originally described the mineral, W. Bruhns and K. Busz (3). More recently phosphosiderite has been described from Kirunavara, Sweden, by R. Koechlin (4).

De Angelis demonstrated that the symmetry is monoclinic on the basis of three different types of evidence:

(1) The etch figures on the basal pinakoid do not exhibit planar symmetry with respect to a plane normal to the a axis, nor axial symmetry with respect to the c axis (Fig. 4).

(2) The goniometric measurements cannot be reconciled with orthorhombic axes of reference, but are quite amenable to monoclinic axes with $\beta = 89^\circ 24'$. Certain prominent faces are not repeated as required by orthorhombic symmetry.

(3) The optical data are not consistent with orthorhombic symmetry, because $X \wedge c > +3^\circ$.

Before the appearance of the work by De Angelis, W. T. Schaller (5) had pointed out the marked similarity between the compositions, crystal habits and axial ratios of phosphosiderite and metavariscite [formerly called variscite (6)] and he had suggested the possibility of an isodimorphous series:

| Octahedral Habit | Tabular Habit |
|------------------|-----------------|
| Scorodite | — |
| Strengite | Phosphosiderite |
| Variscite | Metavariscite |

P. Kokkoros (7) has recently shown that scorodite and strengite are isostructural and the writer has found that variscite produces a powder diffraction pattern sufficiently similar to indicate that it also belongs to this group.

It seemed desirable to investigate phosphosiderite further by means of x -ray methods in order to ascertain whether or not the symmetry is monoclinic¹ and, if possible, to determine its structure.

¹ Although the work of De Angelis gives the appearance of care and precision, a question might arise regarding the identity of the material from Sardinia with that from Pleystein and Eiserfeld. The habit of the mineral from Sardinia is somewhat different and a different optical orientation is reported.

The crystals examined in this study are from Pleystein, Bavaria. They exhibit the forms described by Laubmann and Steinmetz (2), but a number of them show a curved, striated face which is apparently not repeated as would be required by orthorhombic symmetry. Frequently this face, or combination of faces, is quite prominent. Portions of some of the crystals and a few entire crystals are clear and pale rose colored, but many are quite cloudy and bluish-green. The coloration of these crystals is caused by the presence of many inclusions. Because of the prevalence of rounded and striated faces, the crystals do not lend themselves to accurate goniometric measurement. A considerable number of them are twins.

ACKNOWLEDGMENTS

The writer is indebted to the faculty in physics for the use of their laboratories and apparatus. He is particularly indebted to Professor M. Y. Colby for reading the manuscript and for numerous helpful suggestions. Professors F. L. Whitney and Arnold Romberg kindly assisted with the translation of the work by De Angelis. Dr. W. F. Foshag, of the U. S. National Museum, kindly furnished the specimens of phosphosiderite and strengite, scorodite and variscite. Mr. Lynn Gardiner, of the University of Minnesota, kindly prepared the powder diffraction patterns of these specimens.

EXPERIMENTAL DATA

Comparatively little difficulty was encountered in obtaining a Laue photograph in the direction of the b axis. A photograph parallel to a was obtained with considerably greater difficulty because of the thin tabular habit of the crystals and the presence of innumerable inclusions. Both of these photographs indicate the centrosymmetric group C_2^b and demonstrate the proximity of β to 90° (Figs. 1 and 2).

A series of oscillation photographs was prepared using MoK radiation. Intensity estimates, which were obtained from these photographs, greatly facilitated the interpretation of the powder diagram (Table 1). Indeed, many of the ambiguities which would otherwise arise in the interpretation of the powder diagram can only be eliminated through consideration of the data obtained from the Laue and oscillation photographs.

Specimens from Sardinia and Eiserfeld were not available for the present study, but a powder diffraction pattern of the specimen from Pleystein is given and a comparison with samples from other localities can be obtained readily on that basis.

However, the material which De Angelis examined must have been phosphosiderite, in spite of the difference in habit, and numerous reasons for this conclusion will appear in the description of the present results.

The dimensions of the unit cell were ascertained by comparison with a pattern of calcite. The values obtained are:

| Absolute | Ratios | Ratios (De A.) |
|-------------------------------|--------------------------|------------------------|
| $a_0 = 5.30 \text{ \AA}$ | 0.541 | 0.5449 |
| $b_0 = 9.79$ | 1. | 1. |
| $c_0 = 8.67$ | 0.886 | 0.8968 |
| (all $\pm 0.01 \text{ \AA}$) | $[\beta = 89^\circ 24']$ | $\beta = 89^\circ 24'$ |

The methods employed are not sufficiently accurate to permit a precise determination of the angle β when the deviation from 90° is of this order of magnitude. The result obtained by goniometric measurement (1) was used in the calculation of the interplanar distances (Table 1) and the agreement is most excellent.

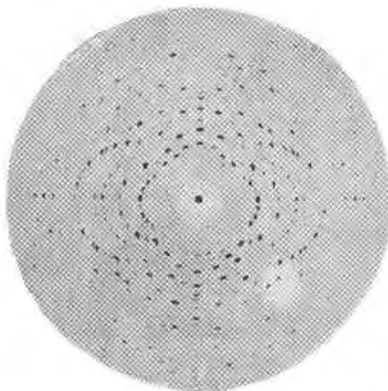


FIG. 1. Laue photograph with incident ray nearly parallel to the b axis, showing axial symmetry of spots, but not planar symmetry.

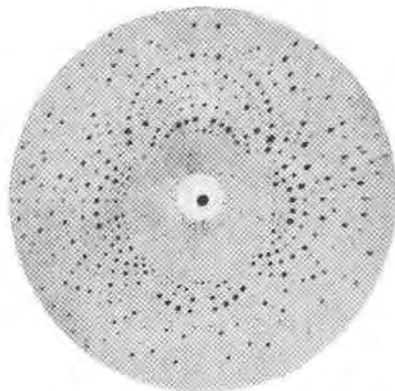


FIG. 2. Laue photograph with incident ray slightly inclined to the a axis.

It was not possible to obtain a sample sufficiently pure to completely exclude extraneous lines from the powder diffraction diagram, and several of the lines given in Table 1 were contributed by strengite, as indicated by *Str.*—the subscripts indicating the relative intensities of these lines in the strengite pattern. One other impurity was also present and three extraneous lines are probably due to this substance, the lines of which are marked *Imp.* This substance was not identified but some of the more likely possibilities were eliminated, including dufrenite, variscite, scorodite, quartz and calcite.

The data obtained by the oscillation method offer confirmation of the interpretation of the Laue photographs, demonstrating that one inclined axis is present, but only one. This is shown in Fig. 3, where certain intensity differences are noticeable. The photographs produced by oscillation about the b axis were symmetrical, except for spots obviously caused by smaller adhering crystals and inclusions.

TABLE 1. POWDER DIAGRAM OF PHOSPHOSIDERITE
(Unfiltered Fe radiation— $r=57.3$ mm.)

| No. | Indices | $d_{calc.}$ | $d_{exp.}$ | $I_{exp.}$ | No. | Indices | $d_{calc.}$ | $d_{exp.}$ | $I_{exp.}$ |
|-----|----------------------------------|--------------------|------------|---------------|-----|--------------|-------------|------------|---------------|
| 1 | <i>Imp.</i> | — | 7.12 | $\frac{1}{2}$ | 35 | 310 | 1.739 | 1.739 | $\frac{1}{2}$ |
| 2 | <i>Imp.</i> | — | 6.75 | $\frac{1}{2}$ | | 30 $\bar{1}$ | 1.735 | | |
| 3 | 011 | 6.49 | 6.48 | 1 | | 13 $\bar{4}$ | 1.713 | | |
| 4 | <i>Str.</i> ₁₁ | — | 5.37 | $\frac{1}{2}$ | 36 | 31 $\bar{1}$ | 1.708 | 1.716 | 3 |
| 5 | β 110 | 5.13 | 5.13 | 1 | | 015 | 1.707 | | |
| 6 | 020 | 4.90 | 4.88 | 1 | 37 | 15 $\bar{2}$ | 1.693 | 1.691 | 1 |
| 7 | β 002 | 4.78 | 4.81 | 1 | | 152 | 1.689 | | |
| 8 | 110 | 4.66 | 4.67 | 5 | 38 | 025 | 1.673 | 1.670 | 3 |
| 9 | 10 $\bar{1}$ | 4.54 | 4.55 | $\frac{1}{2}$ | | 320 | 1.662 | | |
| 10 | { 101 β 111 } | { 4.50 4.50 } | 4.48 | $\frac{1}{2}$ | | 32 $\bar{1}$ | 1.635 | | |
| 11 | 002 | 4.355 | 4.327 | 6 | 39 | 060 | 1.632 | 1.633 | 2 |
| 12 | 111 | 4.090 | 4.089 | 2 | | 11 $\bar{5}$ | 1.630 | | |
| 13 | { 012 β 120 } | { 3.964 3.961 } | 3.965 | 2 | 40 | 321 | 1.629 | 1.603 | $\frac{1}{2}$ |
| 14 | <i>Str.</i> ₂ | — | 3.696 | $\frac{1}{2}$ | | 312 | 1.608 | | |
| 15 | 120 | 3.596 | 3.592 | 5 | 41 | 061 | 1.604 | 1.580 | 2 |
| 16 | 121 | 3.313 | 3.320 | 2 | | 224 | 1.580 | | |
| 17 | { 031 β 013 } | { 3.054 3.053 } | 3.052 | 3 | 42 | 160 | 1.559 | 1.555 | 2 |
| 18 | β 210 | 2.818 | 2.831 | 1 | | 330 | 1.554 | | |
| 19 | { 130 013 } | { 2.779 2.772 } | 2.771 | >10 | 43 | 15 $\bar{3}$ | 1.553 | 1.528 | 3 |
| 20 | 200 | 2.650 | 2.651 | 1 | | 33 $\bar{1}$ | 1.532 | | |
| 21 | 210 | 2.558 | 2.557 | 5 | 44 | 24 $\bar{3}$ | 1.532 | 1.528 | 3 |
| 22 | <i>Imp.</i> | — | 2.502 | $\frac{1}{2}$ | | 035 | 1.531 | | |
| 23 | { 211 113 } | { 2.448 2.447 } | 2.452 | 1 | 45 | 331 | 1.527 | 1.506 | 1 |
| 24 | { 132 220 } | { 2.334 2.331 } | 2.338 | 2 | | 30 $\bar{3}$ | 1.515 | | |
| 25 | { 12 $\bar{3}$ 202 } | { 2.262 2.251 } | 2.256 | 2 | 46 | 303 | 1.500 | 1.492 | 1 |
| 26 | 140 | 2.222 | 2.221 | 2 | | 23 $\bar{4}$ | 1.498 | | |
| 27 | 014 | 2.116 | 2.123 | 3 | 47 | 31 $\bar{3}$ | 1.497 | 1.486 | 1 |
| 28 | { 22 $\bar{2}$ 230 } | { 2.062 2.057 } | 2.064 | 1 | | 234 | 1.486 | | |
| 29 | { 10 $\bar{4}$ 13 $\bar{3}$ } | { 2.013 2.009 } | 2.011 | 5 | 48 | 205 | 1.458 | 1.453 | 1 |
| 30 | { 024 14 $\bar{2}$ } | { 1.982 1.981 } | 1.986 | 1 | | 32 $\bar{3}$ | 1.447 | | |
| 31 | { 051 213 } | { 1.910 1.906 } | 1.912 | 1 | 49 | 006 | 1.445 | 1.439 | 1 |
| 32 | 150 | 1.837 | 1.838 | 1 | | 215 | 1.442 | | |
| 33 | { 223 034 } | { 1.806 1.805 } | 1.813 | 2 | 50 | 323 | 1.434 | 1.406 | 1 |
| 34 | { 14 $\bar{3}$ 24 $\bar{1}$ } | { 1.767 1.763 } | 1.766 | 3 | | 341 | 1.411 | | |
| | | | | | 48 | 15 $\bar{4}$ | 1.404 | 1.406 | 1 |
| | | | | | | 154 | 1.399 | | |
| | | | | | 49 | 106 | 1.398 | 1.392 | 3 |
| | | | | | | 225 | 1.397 | | |
| | | | | | 50 | 106 | 1.390 | 1.376 | 3 |
| | | | | | | 260 | 1.389 | | |
| | | | | | | 25 $\bar{3}$ | 1.387 | | |
| | | | | | | 253 | 1.379 | | |
| | | | | | | 30 $\bar{4}$ | 1.376 | 1.376 | 3 |
| | | | | | | 33 $\bar{3}$ | 1.375 | | |

The absence of (010) was observed for odd orders through the 7th, beyond which the presence or absence could not be ascertained with certainty. However, it is noteworthy that (001) first appears odd with appreciable intensity in the 9th order although it is possibly also present in the 7th, and (100) does not occur in an odd order until the 5th. If the absence of (010) in odd orders is characteristic the possible space groups are C_2^2 and C_{2h}^2 , because the cell is simple monoclinic. If (010) is not characteristically absent in odd orders the possibilities must be extended to include C_s^1 , C_2^1 and C_{2h}^1 .

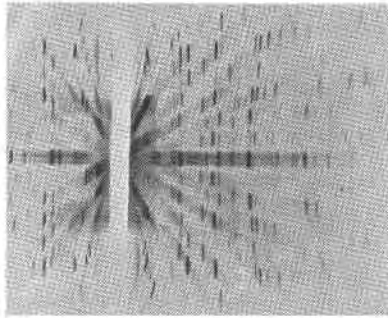


FIG. 3. Oscillation photograph produced by rotation of 20° about the c axis from 100, showing asymmetric intensities of the reflections.

In an attempt to limit further the space group, a number of crystals were etched on (010). The results obtained by etching with HCl were not gratifying. In general these efforts suffered from various sorts of interferences and figures which seemed to indicate planar symmetry were obtained as well as those which indicated axial symmetry. In addition some of the figures appeared to be asymmetric.

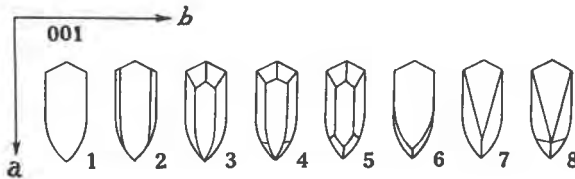


FIG. 4. Etch figures obtained by action of hot HCl on 001 (Redrawn from De Angelis).

The etch figures which De Angelis obtained seem to be more diagnostic than any that were obtained in this study and these are given in Fig. 4. It is highly probable that the symmetry of phosphosiderite is holohedral

because the figures obtained on 001 and $00\bar{1}$ were centrosymmetric, and there can be little doubt concerning the planar symmetry of these figures.

If it can now be concluded that the symmetry is holohedral and that (010) reflections are absent in the higher odd orders (above the 8th order) as well as in the lower orders the space group is C_{2h}^2 . If the symmetry is not holohedral C_2^2 is also a possibility, and if the odd high order reflections of (010) are not absent, C_{2h}^1 must be considered. Nevertheless, the space group is limited to five possibilities through consideration of the reflections which are definitely present.

The most probable formula that has been suggested for phosphosiderite is $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$. Using this as a basis for calculating the density gives

$$\rho = \frac{4 \times 1.649 \times 186.9}{5.30 \times 8.67 \times 9.79 \times \sin 89^\circ 24'} = 2.74$$

The only recorded value for the specific gravity is 2.76, which agrees sufficiently well with the *x*-ray measurements and enhances the probability of this formula.

W. H. Zachariasen (8) was able to obtain an unique solution for a structure having the space group C_{2h}^2 and requiring the determination of sixteen parameters, but the analysis was irrelevant and involved a consideration of the intensities of some 700 reflections. The photographs obtained in the present study will not permit the assignment of indices and intensities to a large number of reflections. Under these circumstances it does not seem feasible to determine the structure by any straightforward method.

SUMMARY

Phosphosiderite is monoclinic and probably holohedral, in which case the space group is C_{2h}^2 or C_{2h}^1 . The apparent absence of (010) in odd orders recommends C_{2h}^2 . The value $\beta = 89^\circ 24'$ obtained by goniometric measurement (1) agrees excellently with the *x*-ray data. Other lattice constants are: $a_0 = 5.30$, $b_0 = 9.79$ and $c_0 = 8.67$ (all ± 0.01 Å). The unit cell contains four molecules of $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$, yielding a theoretical density 2.74.

A powder diffraction pattern has been interpreted through the aid of Laue and oscillation photographs, and these measurements should prove useful in ascertaining which minerals are isostructural with phosphosiderite. The unfavorable geometry impedes a determination of the structure from the data obtainable.

REFERENCES

1. DE ANGELIS, M., Intorno alla forma cristallina della fosfosiderite di S. Giovanneddu presso Gonnese in Sardegna: *Annali del Museo Civico di St. Nat. di Genova*, **52**, 138-148 (1926).
2. LAUBMANN, H., and STEINMETZ, H., Phosphatführende Pegmatite des Oberpfälzer und Bayerischen Waldes: *Zeits. Krist.*, **55**, 523-586 (1920).
3. BRUHNS, W., and BUSZ, K., Phosphosiderit, ein neues Mineral von der Grube Kalterborn bei Eiserfeld im Siegenschen: *Zeits. Krist.*, **17**, 555-560 (1890).
4. KOEHLIN, R., Mineralogische Nachlese: *Centrb. Mineral.*, [A] **1934**, 256-266 and 289-298.
5. SCHALLER, W. T., Lucinite, a new mineral: a dimorphous form of variscite. Mineralogical Notes, Series 3, *U. S. G. S., Bull.* **610**, 56-68 (1916).
6. LARSEN, E. S., and SCHALLER, W. T., The identity of variscite and peganite and the dimorphous form, metavariscite: *Am. Mineral.*, **10**, 23-28 (1925).
7. KOKKOROS, P., Vergleichende röntgenographische Untersuchung von Arsenaten und Selenaten (Skorodit, Strengit, Cadmiumselenat-Dihydrat und Manganoselenat-Dihydrat): *Prakt. Acad. Athènes*, **13**, 337-344 (1938).
8. ZACHARIASEN, W. H., Crystal lattice of potassium pyrosulphite, $K_2S_2O_5$, and the structure of the pyrosulphite group: *Phys. Rev.*, **40**, 923-935 (1932).