

Phase Determination for Colemanite, $\text{CaB}_3\text{O}_4(\text{OH})_3 \cdot \text{H}_2\text{O}$

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(Received 24 January 1958)

The procedures used to calculate the signs of the structure factors for colemanite, a $P2_1/a$ crystal, are described in some detail. The F_{obs}^2 are adjusted for vibrational motion and put on an absolute scale. From the corrected F_{hkl}^2 , the magnitudes of the normalized structure factors E_{hkl} are calculated, and the signs of these determined by the application of the Σ_1 , Σ_2 , and Σ_3 formulas of Monograph I of Hauptman & Karle (1953).

Introduction

A general procedure for phase determination applicable to centrosymmetric space groups has already been described (Hauptman & Karle, 1953, hereafter referred to as Monograph I). We here describe in detail the application of these procedures to the determination of the signs of the structure factors for colemanite, a $P2_1/a$ crystal. The crystal structure of colemanite was given in a preliminary way in 1954 (Christ, Clark & Evans), and is described in detail in an accompanying paper (Christ, Clark & Evans, 1958).

Adjustment of F_{obs}^2

The 3084 independent observed intensities corrected for Lorentz factor, and polarization, F_{obs}^2 , were further corrected for vibrational motion and placed on an absolute scale by a method previously described (Wilson, 1949; Karle & Hauptman, 1953). First we computed

$$\sigma_2 = \sigma_2(s) = \sigma_2(h, k, l) = \sum_{j=1}^N f_j^2(h, k, l), \quad (1)$$

where $s = \sin \theta / \lambda$, f_j is the atomic structure factor, and N is the number of atoms in the unit cell. For colemanite, the unit cell consists of $4[\text{CaB}_3\text{O}_4(\text{OH})_3 \cdot \text{H}_2\text{O}]$, and $N = 68$. Next we define

$$\left. \begin{aligned} \varepsilon = \varepsilon(s) = \varepsilon_{hkl} = 2 \text{ if } k = 0 \text{ or if } h = l = 0, \\ \varepsilon = \varepsilon(s) = \varepsilon_{hkl} = 1 \text{ otherwise.} \end{aligned} \right\} (2)$$

The s values were arranged in increasing order and the values of s , ε , σ_2 and F_{obs}^2 were tabulated. The s range was divided into 16 intervals in each of which there occur 200 F_{obs}^2 values, except that in the first interval only 84 F_{obs}^2 values appear. For each of these 16 intervals the following number was computed

* Publication authorized by the Director, U.S. Geological Survey.

† There are of course only 84 s values in the first interval.

$$K = \frac{\sum \varepsilon \sigma_2}{\sum F_{\text{obs}}^2} \quad (3)$$

where the sums are extended over the 200† s (or h, k, l) values appearing in the interval. We label each interval by the s value at its center so that K appears as a function of s . In this way 16 points were obtained and are shown in Fig. 1 as circles. Finally, the smooth monotonically increasing curve $K(s)$ was drawn among these points. The same procedure was carried out using 11 intervals with 300 s values per interval, and the corresponding points appear as crosses in Fig. 1. The

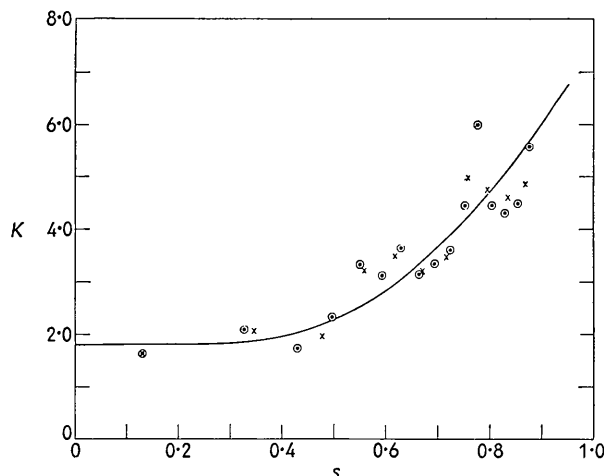


Fig. 1. K curve for colemanite.

smooth monotonically increasing curve drawn among these 11 points coincides with the $K(s)$ curve previously obtained. Finally, by means of

$$F_{hkl}^2 = F_{\text{obs}}^2 K(s) \quad (4)$$

we obtained the values of the F_{hkl}^2 corrected for vibrational motion and placed on an absolute scale which are needed to compute the E_{hkl}^2 in the next section.

$$\sum_k = \sum_{h,l} (-1)^{h+k} (E_{hkl}^2 - 1). \quad (14)$$

Tentative signs for the first 150 of these were obtained from

Table 2. Values of $\sum_k = \sum_{h,l} (-1)^{h+k} (E_{hkl}^2 - 1)$

| k | \sum_k | k | \sum_k |
|-----|----------|-----|----------|
| 0 | 13 | 8 | -75 |
| 1 | -251 | 9 | 39 |
| 2 | 102 | 10 | 32 |
| 3 | -61 | 11 | -76 |
| 4 | -53 | 12 | 63 |
| 5 | 87 | 13 | -60 |
| 6 | -114 | 14 | 42 |
| 7 | 105 | 15 | -28 |

$$\sum'_{3i} = \sum_{j=1}^{30} E_{h_j 0 l_j} (E_{h_\mu k_\mu l_\mu}^2 - 1), \quad (17)$$

where the signs of the 30 $E_{h_j 0 l_j}$ (with h_j and l_j both even) have already been determined,

$$h_\mu = \frac{1}{2}(h_i \pm h_j), \quad k_\mu = \frac{1}{2}k_i, \quad l_\mu = \frac{1}{2}(l_i \pm l_j), \quad (18)$$

and the upper (lower) signs in (18) go together. In view of Case 6, Table 11 of Monograph I, the sign of $E_{h_i k_i l_i}$ where h_i, k_i, l_i are all even is the sign of \sum'_{3i} . Final signs for all 244 $E_{h_i k_i l_i}$ with h_i, k_i, l_i all even, were then obtained by means of

$$\sum''_{3i} = \sum_j [E_{h_j k_j l_j} \sum_{k_\mu} (-1)^{h_\mu + k_\mu} (E_{h_\mu k_\mu l_\mu}^2 - 1)], \quad (19)$$

where

$$\left. \begin{aligned} k_j &= k_i \\ h_\mu &= \frac{1}{2}(h_i \pm h_j), \quad l_\mu = \frac{1}{2}(l_i \pm l_j), \end{aligned} \right\} \quad (20)$$

The signs of the E_{g0g}
 There are 44 E_{g0g} . In view of Case 1, Table 10 of Monograph I, the sign of E_{h0l} where h and l are both even is the sign of $\sum_{\frac{h}{2}}^l$ and may therefore be read directly from Table 1. However, not all the signs were decisively determined. In order to determine these 44 signs without question as well as to test the internal consistency of the method, Case 2, Table 11 of Monograph I was applied. The E_{g0g} were arranged in decreasing order of magnitude and labelled with an index i ranging from 1 to 44. It was assumed that the first 15 signs were correctly obtained from Table 1. Then to obtain the sign of $E_{h_i 0 l_i}$ we computed*

the upper (lower) signs in (20) go together, and the $E_{h_i k_i l_i}$ range over several of the 150 E_{ggg} whose signs have already been determined. In view of Case 5, Table 11 of Monograph I, the sign of $E_{h_i k_i l_i}$, where h_i, k_i, l_i are even, is the sign of \sum'_{3i} . We note again that the term \sum of (19) has already been tabulated

$$\sum_{3i} = \sum_{j=1}^{15} [E_{h_j 0 l_j} \sum_{k_\mu} (-1)^{h_\mu + k_\mu} (E_{h_\mu k_\mu l_\mu}^2 - 1)], \quad (15)$$

where the sign of \sum_{3i} is the sign of $E_{h_i 0 l_i}$ and the signs of the fifteen $E_{h_j 0 l_j}$ are already known,

$$h_\mu = \frac{1}{2}(h_i \pm h_j), \quad l_\mu = \frac{1}{2}(l_i \pm l_j), \quad (16)$$

k_μ takes on the value zero only if h_μ is even, the upper (lower) signs in (16) go together, and $j \neq i$. The term \sum of (15) has already been tabulated in Table 1.

The signs of the first 15 $E_{h_i 0 l_i}$ agreed with those previously determined. In fact among all 44 of the $E_{h_i 0 l_i}$ only 5 discrepancies occurred between summary Table 1 and \sum_{3i} . These were all resolved in favor of \sum_{3i} .

In Table 1. Although not all 244 signs were decisively determined, it was felt that a sufficient number of signs were obtained to render unnecessary a further application of (19). In view of the space-group symmetry, $E_{hkl} = E_{h\bar{k}l} = E_{h\bar{k}\bar{l}} = E_{h\bar{l}\bar{k}}$ for h and k both even. Hence the signs of some 700 E_{ggg} in addition to the 244 listed E_{ggg} are available for use in the later stages of the procedure if needed.

The signs of the E_{guu}

Among the remaining E_{hkl} , all of whose phases are linearly independent modulo two, the one having the largest normalized structure factor magnitude is $E_{12,1,3}$ for which $|E_{12,1,3}| = 4.71$. In accordance with Step 2, p. 47, of Monograph I, the sign of $E_{12,1,3}$ may be arbitrarily specified. We chose $E_{12,1,3} = +4.71$ and proceeded to find the signs of the remaining E_{guu} , whose phases are linearly dependent modulo two on that of $E_{12,1,3}$. First the $E_{12,u,3}$ were arranged in decreasing order of magnitude and labelled with the index i . Then we computed, for each fixed $i > 1$,

The signs of the E_{0g0}

There are 7 E_{0g0} . In view of Case 1, Table 10 of Monograph I, the sign of E_{0k0} where k is even is the sign of $\sum_{\frac{k}{2}}$ and may therefore be read directly from Table 2. In this case all 7 signs were so decisively determined that it was not felt necessary to re-determine them independently, as was done for the E_{g0g} .

$$\sum'_{3i} = \sum_{j < i} \mp [E_{h_j k_j l_j} \sum_{h_\mu l_\mu} (-1)^{h_\mu + k_\mu} (E_{h_\mu k_\mu l_\mu}^2 - 1)], \quad (21)$$

where

$$h_j = 12, \quad l_j = 3, \quad (22)$$

$$k_\mu = \frac{1}{2}(k_i \pm k_j), \quad (23)$$

The signs of the E_{ggg}

There are 244 E_{ggg} . These were arranged in decreasing order of magnitude and labelled with the index i .

the upper (lower) signs in (21) and (23) go together, k_j ranges over the odd integers, and the signs of the $E_{h_j k_j l_j}$ are assumed to be known. We note that the

* Equation (15) contains only 14 summands when $i \leq 15$.

term \sum of (21) is tabulated in Table 2. In view of Case 5, Table 11 of Monograph I, the sign of $E_{h_i k_i l_i}$ is the sign of Σ'_{3i} . If $i = 2$, j takes on only the value 1, but as more and more signs become known j ranges over larger and larger numbers.

Once the signs of all the $E_{12,u,3}$ were determined we proceeded to find the signs of the remaining E_{guu} . For each fixed odd k we arranged the E_{gku} in decreasing order of magnitude and labelled the indices with the index i . For each fixed $h_i k_i l_i$ of type guu we computed

$$\Sigma'_{3i} = \sum_{j < i} \mp [E_{h_j k_j l_j} \sum_{k_\mu} (-1)^{h_\mu + k_\mu} (E_{h_\mu k_\mu l_\mu}^2 - 1)], \quad (24)$$

where

$$k_j = k_i, \quad (25)$$

$$h_\mu = \frac{1}{2}(h_i \pm h_j), \quad (26)$$

$$l_\mu = \frac{1}{2}(l_i \pm l_j), \quad (27)$$

the upper (lower) signs in (24), (26), and (27) go together, h_j is even, l_j is odd, and the signs of the $E_{h_j k_j l_j}$ are assumed to be known. Again the term \sum of (24) is tabulated in Table 1. In view of Case 5, Table 11 of Monograph I, the sign of $E_{h_i k_i l_i}$ is the sign of Σ'_{3i} . If $i = 2$, j takes on only the value 1, but as more and more signs become known j ranges over larger and larger numbers. However, it was rarely found necessary for j to range over more than ten values. In this way for each fixed odd k value the signs of the $E_{h_i k_i l_i}$ of type E_{guu} were found. Again most but not all of the signs were decisively determined. It was not felt desirable to apply any additional formulas at this stage of the procedure. Again due to the space-group symmetry

$$E_{hkl} = -E_{\bar{h}\bar{k}\bar{l}} = -E_{\bar{h}k\bar{l}} = E_{\bar{h}\bar{k}l}$$

if h is even and k is odd. Hence the knowledge of the signs of the listed E_{guu} implies a knowledge of the signs of roughly 700 additional E_{guu} which are available for later use.

The signs of the E_{uuu}

Among the remaining E_{hkl} , all of whose phases are linearly independent modulo two of any phase φ_{guu} , the one having the largest normalized structure factor magnitude is E_{953} for which $|E_{953}| = 3.71$. In accordance with Step 3, p. 48, of Monograph I, the sign of E_{953} may be arbitrarily specified. We chose $E_{953} = +3.71$ and proceeded to find the signs of the remaining E_{uuu} , whose phases are linearly dependent modulo two on that of E_{953} . This was done exactly as in the previous section except that (21) and (24) were replaced by

$$\Sigma'_{3i} = \sum_{j < i} [E_{h_j k_j l_j} \sum_{h_\mu, l_\mu} (-1)^{h_\mu + k_\mu} (E_{h_\mu k_\mu l_\mu}^2 - 1)] \quad (28)$$

and

$$\Sigma''_{3i} = \sum_{j < i} [E_{h_j k_j l_j} \sum_{k_\mu} (-1)^{h_\mu + k_\mu} (E_{h_\mu k_\mu l_\mu}^2 - 1)] \quad (29)$$

respectively in accordance with Case 5, Table 11, of Monograph I.

The signs of the E_{gug}

Among those of the remaining E_{hkl} whose phases φ_{hkl} are linearly independent modulo two of the pair $\varphi_{12,1,3}$, φ_{953} the one having the largest normalized structure factor magnitude is $E_{14,1,0}$ for which $|E_{14,1,0}| = 3.61$. In accordance with Step 4, p. 48, of Monograph I, the sign of $E_{14,1,0}$ may be arbitrarily specified. We chose $E_{14,1,0} = +3.61$ and proceeded to find the signs of the remaining E_{gug} , whose phases are linearly dependent modulo two on that of $E_{14,1,0}$. These were obtained in exactly the same way as those of the E_{guu} .

The signs of the E_{ugg}

The phases which are linearly dependent modulo two on the pair $\varphi_{12,1,3}$, φ_{953} are of the type φ_{ugg} . In accordance with Step 5, p. 49, of Monograph I, the signs of all the E_{ugg} are determined by those chosen for $E_{12,1,3}$ and E_{953} . For each fixed even k the E_{hkl} with h odd and l even were arranged in decreasing order of magnitude and labelled with the index i . Then we computed, for each of some 10 or 12 values of i

$$\Sigma_{2i} = \sum_{\mu, \nu} E_{h_\mu k_\mu l_\mu} E_{h_\nu k_\nu l_\nu}, \quad (30)$$

where

$$\mathbf{h}_i = \mathbf{h}_\mu \pm \mathbf{h}_\nu. \quad (31)$$

$E_{h_\mu k_\mu l_\mu}$ is of type E_{guu} , $E_{h_\nu k_\nu l_\nu}$ is of type E_{uuu} , and $E_{h_i k_i l_i}$ is of type E_{ugg} . Hence the signs of the $E_{h_\mu k_\mu l_\mu}$ and the $E_{h_\nu k_\nu l_\nu}$ had already been computed. In view of Step 5, p. 49, of Monograph I, the sign of $E_{h_i k_i l_i}$ is the sign of Σ_{2i} . Although (30) may contain several hundred terms, by restricting attention to those terms for which $|E_{h_\mu k_\mu l_\mu}|$ and $|E_{h_\nu k_\nu l_\nu}|$ were large, it was found to be sufficient to retain only six or eight summands in (30). Although (30) could have been used to obtain the signs of all the E_{ugg} it proved convenient to obtain the signs of only ten or twelve of these for each fixed even integer k . Then equation (24) was used to obtain the signs of all the remaining E_{ugg} with the same middle index k .

The signs of the E_{ggu}

The phases which are linearly dependent modulo two on the pair $\varphi_{12,1,3}$, $\varphi_{14,1,0}$ are of the type E_{ggu} . In accordance with Step 6, p. 49, of Monograph I, the signs of all the E_{ggu} are determined by those chosen for $E_{12,1,3}$ and $E_{14,1,0}$. The procedure is the same as that used for the E_{ugg} except that in the latter part of the procedure equation (29) was used instead of equation (24). To justify the procedure for the E_{ggu} reference should be made to Case 2, Table 11, of Monograph I rather than to Case 5.

The signs of the E_{ugu}

The phases which are linearly dependent modulo two on the pair φ_{953} , $\varphi_{14,1,0}$ are of the type E_{ugu} . In accordance with Step 7, p. 49, of Monograph I, the signs of all the E_{ugu} are determined by those chosen for E_{953} and $E_{14,1,0}$. The procedure is the same as that used for the E_{ugg} .

The signs of the E_{uug}

The only phases which remain are those which are linearly dependent modulo two on the triple $\varphi_{12,1,3}$, φ_{953} , $\varphi_{14,1,0}$, i.e. those of type φ_{uug} . Although all these phases could have been determined by means of Σ_2 as recommended in Step 8, p. 49, of Monograph I, it was again found convenient to use Σ_2 to determine only a few of the φ_{uug} . Then, as in determining the signs of the E_{ugg} , equation (29) was used to find all remaining signs.

Concluding remarks

Owing to the large number of data relative to the number of atomic parameters to be determined, the initial probabilities associated with the sign deter-

mining formulas were very high and thus the simple procedure described for colemanite proved adequate. In a less favorable case, it would have been necessary to correlate the phase determining procedure more closely with the corresponding probabilities.

Since this structure determination was carried out, new phase determining formulas making use of algebraic and probability methods (Hauptman & Karle, 1957, 1958; Karle & Hauptman, 1957) have been obtained. These new procedures will ultimately supersede the one described in this paper.

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Studies of Borate Minerals (III): The Crystal Structure of Colemanite, $\text{CaB}_3\text{O}_4(\text{OH})_3 \cdot \text{H}_2\text{O}^*$

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(Received 13 February 1958)

Colemanite, $\text{CaB}_3\text{O}_4(\text{OH})_3 \cdot \text{H}_2\text{O}$, is monoclinic, $P2_1/a$, with $a = 8.743 \pm 0.004$, $b = 11.264 \pm 0.002$, $c = 6.102 \pm 0.003$ Å, $\beta = 110^\circ 7'$, $Z = 4$. Signs for 1997 of the observed reflections were calculated by the statistical method of Hauptman & Karle (1953). The $\rho(x, y, z)$ using the structure factors for which $(\sin \theta)/\lambda \leq 0.66$ Å⁻¹ established the preliminary structure. This structure was refined by electron-density projections, least-squares analysis, and final three-dimensional electron-density mapping. Colemanite contains infinite chains along a , linked together laterally by ionic bonds through Ca^{++} ions to form sheets parallel to (010). The sheets, in turn, are linked together through a system of hydrogen bonds involving the hydroxyl groups of the chains and water molecules. The chain element has the composition $[\text{B}_3\text{O}_4(\text{OH})_3]^{-2}$ and consists of a BO_3 triangle, a $\text{BO}_3(\text{OH})$ tetrahedron, and a $\text{BO}_2(\text{OH})_2$ tetrahedron linked at corners to form a ring. Considerations of the electrical properties of colemanite in terms of its structure indicate that the hydrogen atoms are disordered at room temperature and become ordered at the transition of colemanite to a ferroelectric phase. A comparison of the signs calculated by the Hauptman-Karle method with those calculated from the final structure shows that for the 1809 determinate signs (188 were indeterminate), 9.5% were wrong by the statistical method. Approximately one-third of the wrong signs were those for principal-zone reflections.

Introduction

As part of a systematic investigation of the crystal structures of borate minerals, the series

$2\text{CaO} \cdot 3\text{B}_2\text{O}_3 \cdot x\text{H}_2\text{O}$ is being studied. In this series x has the following values: for colemanite $x = 5$, for meyerhofferite $x = 7$, for a synthetic compound $x = 9$, and for inyoite $x = 13$. The compound for which $x = 11$ is not known to exist. Preliminary descriptions of the crystal structures of colemanite (Christ,

* Publication authorized by the Director, U.S. Geological Survey.