

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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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,

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Clark & Evans, 1954), meyerhofferite (Christ & Clark, 1956), and of the synthetic compound (Clark & Christ, 1957) have been given. The crystal structure of inyoite has recently been solved (Joan R. Clark, private communication).

The solution of the crystal structure of colemanite constituted the first test of the direct method of crystal structure determination of Hauptman & Karle (1953) for an unknown structure. In the present paper a detailed description of the structure of colemanite is given. The details of the calculations for the determination of the signs of the structure factors, following the statistical procedure of Hauptman & Karle, are given in an accompanying paper (Karle, Hauptman & Christ, 1958).

Experimental work

Crystal description, space group, and unit-cell dimensions

The crystals of colemanite used came from Meyerhofferite Tunnel in Twenty Mule Team Canyon, Death Valley, Inyo County, California, U.S.A.; they are small, colorless, transparent, prismatic elongated along [001], with large {110}. The space group, lattice constants, and powder data for colemanite have been reported previously (Christ, 1953). A new method of obtaining lattice constants of moderately high precision, using the conventional Weissenberg goniometer, was employed in the 1953 study of colemanite. This method has since been described elsewhere (Christ, 1956). For completeness in the present paper the crystallographic data for colemanite are repeated below:

Monoclinic; space group: $P2_1/a-C_{2h}^5$.

$a=8.743\pm 0.004$, $b=11.264\pm 0.002$, $c=6.102\pm 0.003$ Å;
 $\beta = 110^\circ 7' \pm 5'$.

(Cu radiation: $K\alpha_2\lambda = 1.54434$, $K\alpha_1\lambda = 1.54050$,
 $K\beta\lambda = 1.39217$ Å;

Ag: $a = 4.0861$ Å (calibration standard)).

Cell contents: $4[\text{CaB}_3\text{O}_4(\text{OH})_3\cdot\text{H}_2\text{O}]$.

Density (calc.) = 2.419 g.cm.⁻³, density (obs.) =
 2.42 g.cm.⁻³.

Intensity measurements

For the intensity measurements multiple-film Weissenberg patterns using Mo/Zr radiation were prepared. Three films interleaved with 0.0005 in. Ni foil were used for each exposure. Patterns were made around [010] for the levels $k = 0$ to $k = 15$, inclusive, around [001] for the levels $l = 0$ to $l = 6$, inclusive, and around [100] for the levels $h = 0$ and $h = 1$. Exposure times were of the order of 70 hours at 50 kV. and 20 ma. for each level. In addition, suitably shorter exposures were made for the lower levels, in order to bring the stronger reflections into the range of measurement. Those reflections that could not be recorded in the

Weissenberg camera using Mo/Zr radiation, because of their small Bragg angles, were obtained with Cu/Ni radiation. The intensities were estimated visually by comparison with a standard spot strip of intensities, prepared in the usual way, using a colemanite crystal. Controlled exposures on the standard strip were made so that the intensity of the n th spot is given by $I_n = I_0(2)^{n/2}$, where I_0 corresponds to a barely perceptible blackening of the film. The I_{hkl} 's contained in the reciprocal sphere of radius $(\sin \theta)/\lambda = 0.9$ Å⁻¹ were examined. Of the 3084 non-equivalent reflections (excluding space group extinguished reflections) corresponding to this sphere, 1056 reflections were observed to have intensities below the limit of observation. The estimated intensities were corrected for Lorentz and polarization factors to obtain the $|F_{hkl}|^2$'s. For this correction the $1/Lp$ factor was calculated for each reciprocal lattice point, as a function of its cylindrical coordinates, by IBM methods. The $|F_{hkl}|^2$'s obtained from the several films were all put on the same relative scale by the use of appropriate film factors. Though the use of the triple-film technique and long and short exposures, a range of $|F_{hkl}|^2$ of from 1 to about 10,000 was obtained.

Care was taken to use, for the collection of intensity data, small and as nearly equant crystals as possible (about 0.2 mm. on edge). No corrections for absorption effects were attempted. Under the experimental conditions used, these corrections would, in any case, be small. Similarly, no corrections for variations in spot shape over the various levels were made.

Other considerations

At all stages of the analysis the observed and calculated structure factors were related by use of the scaling constant k , where $k\Sigma|F_o| = \Sigma|F_c|$. The initial three-dimensional electron-density series was put on an approximately absolute scale by multiplying the F_{hkl} 's by the square root of the value of the intercept at $s = (\sin \theta)/\lambda = 0$ of the $K(s)$ curve (Karle & Hauptman, 1953) constructed for colemanite (Karle *et al.*, 1958).

The method of Wilson (1942) was used to determine the values of the isotropic temperature factor. Atomic scattering curves were constructed for Ca⁺² and O⁻² from the values listed by Viervoll & Ögrim (1949) for the neutral atoms. In the case of O⁻², for $(\sin \theta)/\lambda \geq 0.2$ Å⁻¹, the Viervoll-Ögrim values, and for $(\sin \theta)/\lambda < 0.2$ Å⁻¹, the Hartree values were used (*International Tables*, 1935). For Ca⁺² the curve corresponding to the Viervoll-Ögrim values for Ca for $(\sin \theta)/\lambda \geq 0.15$ Å⁻¹ and smoothed in to $f = 18$ at $(\sin \theta)/\lambda = 0$ was used. The Viervoll-Ögrim values for boron were used as given. For convenience in calculation, the f -values for O⁻² were used for all oxygen atoms including those contained in the water molecule and in the hydroxyl groups.

Maxima on the electron-density projections were

located by the method of Booth (1948). The maxima of the initial three-dimensional electron-density function were determined by graphical methods and those of the final three-dimensional series by least-squares fitting to a three-dimensional ten parameter Gaussian function according to the method of Schomaker & Shoemaker, as described in Shoemaker, Donohue, Schomaker & Corey (1950). The actual calculations were carried out following the procedure suggested by Frasson (1955).

Determination and refinement of the structure

The structural problem consists in determining the parameters of one Ca, three B, and eight O (including

OH or H₂O) in the positions 4(e) of the space group $P2_1/a$. The observed absolute F_{hkl} 's of 944 terms, together with their signs as calculated by the statistical procedure of Hauptman & Karle (1953), were used to evaluate electron-density sections over the xz plane at intervals of $\frac{1}{80}$ for $y = 0$ to $y = \frac{1}{4}$. The 944 terms used are those contained within a sphere of radius $(\sin \theta)/\lambda = 0.66 \text{ \AA}^{-1}$. In order to minimize termination-of-series effects, an artificial temperature factor $\exp[-B(\sin \theta/\lambda)^2]$, with $B = 2.5 \text{ \AA}^2$ was multiplied into the observed F_{hkl} 's.

The three-dimensional electron-density map obtained is reproduced from the earlier paper of Christ *et al.* (1954) in Fig. 1. This map immediately revealed

Table 1. Atomic positional parameters for $\text{CaB}_3\text{O}_4(\text{OH})_3 \cdot \text{H}_2\text{O}$

Parameters	Stage of refinement*						
	(1)	(2)	(3)	(4)	(5)	(6) (final)	
Ca	x	0.636	0.635	0.635	0.6343	0.6348	0.6345
	y	0.213	0.212	0.212	0.2116	0.2109	0.2112
	z	0.737	0.739	0.736	0.7371	0.7364	0.7366
O ₁	x	-0.023	-0.020	-0.020	-0.020	-0.017	-0.018
	y	0.250	0.250	0.250	0.248	0.247	0.247
	z	0.312	0.316	0.313	0.312	0.315	0.314
O ₂	x	0.188	0.188	0.188	0.187	0.188	0.188
	y	0.240	0.234	0.234	0.234	0.231	0.233
	z	0.133	0.146	0.142	0.139	0.138	0.139
O ₃	x	-0.078	-0.080	-0.080	-0.081	-0.078	-0.080
	y	0.165	0.165	0.165	0.165	0.164	0.164
	z	-0.068	-0.060	-0.061	-0.070	-0.071	-0.071
O ₄	x	0.342	0.342	0.342	0.344	0.344	0.344
	y	0.148	0.151	0.151	0.150	0.148	0.149
	z	0.503	0.517	0.517	0.508	0.511	0.510
O ₅	x	0.095	0.089	0.089	0.089	0.087	0.088
	y	0.055	0.054	0.054	0.054	0.056	0.055
	z	0.270	0.273	0.270	0.266	0.272	0.270
O ₆	x	0.290	0.301	0.301	0.299	0.297	0.298
	y	-0.067	-0.067	-0.067	-0.067	-0.066	-0.066
	z	0.508	0.506	0.508	0.509	-0.505	0.506
O ₇	x	0.167	0.173	0.173	0.165	0.166	0.165
	y	0.075	0.077	0.077	0.078	0.077	0.078
	z	0.688	0.694	0.695	0.703	0.698	0.699
O ₈	x	0.633	0.624	0.624	0.618	0.613	0.616
	y	0.008	0.018	0.018	0.019	0.017	0.018
	z	0.733	0.903	0.900	0.902	0.898	0.900
B ₁	x	0.358	0.358	0.336	0.335	0.338	0.336
	y	0.208	0.208	0.210	0.212	0.213	0.212
	z	0.297	0.297	0.323	0.314	0.316	0.315
B ₂	x	0.023	0.023	0.031	0.039	0.041	0.040
	y	0.200	0.200	0.182	0.177	0.171	0.174
	z	0.132	0.132	0.148	0.157	0.162	0.160
B ₃	x	0.208	0.208	0.210	0.217	0.221	0.219
	y	0.058	0.058	0.057	0.050	0.053	0.052
	z	0.483	0.483	0.483	0.484	0.498	0.493
R†	(0kl)	0.30	0.18	0.17	0.14	—	—
	(hkl)	0.25	0.18	0.18	0.14	—	—
	(hkl)	—	—	—	0.19	—	—
B‡	(0kl)	—	1.20	1.18	1.02	—	—
	(hkl)	0.66	0.77	0.75	0.73	—	—
	(hkl)	—	—	—	0.93	—	—

* See text for description of stage of refinement. † Residual factor; ΔF omitted in calculation if $F_{\text{obs}} = 0$.

‡ Average isotropic temperature coefficient (in \AA^2).

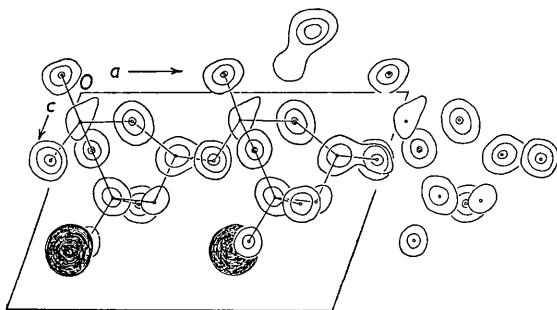


Fig. 1. Composite projection on (010) of the electron-density sections for colemanite. Only a portion sufficient to show the essential features of the structure is given. The small black circles indicate the boron atoms, the small open circles the oxygen atoms. Taken from Christ *et al.* (1954).

the structure of colemanite as consisting of infinite boron-oxygen chains running parallel to the a -axis, with the chain element composed of two BO_4 tetrahedra and a BO_3 triangle sharing corners to form a ring. From a knowledge of the chemical composition of colemanite ($2\text{CaO} \cdot 3\text{B}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$), and crystal-chemical considerations, it also followed immediately that the infinite chain composition is $[\text{B}_3\text{O}_4(\text{OH})_3]_n^{2n-}$, and that the formula for colemanite should be written $\text{CaB}_3\text{O}_4(\text{OH})_3 \cdot \text{H}_2\text{O}$.

Atomic coordinates were assigned to all twelve atoms in the asymmetric unit from the positions of the maxima of the preliminary three-dimensional electron-density map. These coordinates are listed in column (1) of Table 1, which gives the coordinates, residual factor R , and average isotropic temperature factor B , found at each stage of the refinement. Signs calculated on the basis of these coordinates permitted the evaluation of a $\rho_x(y, z)$, using 97 terms out of a possible 119, and a $\rho_z(x, y)$, using 157 terms out of a possible 171.

The maxima of $\rho_z(x, y)$ were always much better resolved than those of $\rho_x(y, z)$ in this and subsequent projections. Consequently, y coordinates were taken from the $\rho_z(x, y)$. This lack of resolution also resulted in z coordinates that were somewhat less accurate than the corresponding x and y coordinates. The set of atomic coordinates chosen at this stage of refinement is given in column (2), Table 1.

Signs calculated on the basis of the coordinates given in column (2), Table 1, were used to calculate a second $\rho_x(y, z)$, using 112 terms out a possible 119, and a second $\rho_z(x, y)$, using 168 terms out of a possible 171. The second $\rho_z(x, y)$ map did not differ significantly from the first one. At this stage a 'best' set of atomic parameters was chosen in the following way: the x and y coordinates of all of the atoms were taken from the first $\rho_z(x, y)$, the z coordinates of the calcium and oxygen atoms were taken from the second $\rho_x(x, z)$, and the z coordinates of the boron atoms re-estimated from the preliminary three-dimensional map. This 'best' set of atomic parameters is given in column (3),

Table 1. One cycle of least-squares refinement was then carried out, using the coordinates of column (3), Table 1, for the $hk0$ and $0kl$ zones. In this analysis unweighted coefficients were used, and nondiagonal terms neglected.

The set of coordinates resulting from the application of the corrections to the coordinates of column (3), Table 1, as indicated by the least-squares analysis, are listed in column (4), Table 1. The coordinates of column (4), Table 1, were used to calculate signs for a final three-dimensional electron-density map. For this map, 2003 of the possible 2028 $F_{\text{obs.}} > 0$, contained within the sphere of reflection of radius $(\sin \theta)/\lambda = 0.9 \text{ \AA}^{-1}$, were included in the calculation. The resulting three-dimensional electron-density map is shown in Fig. 2. The maxima of this map were determined by

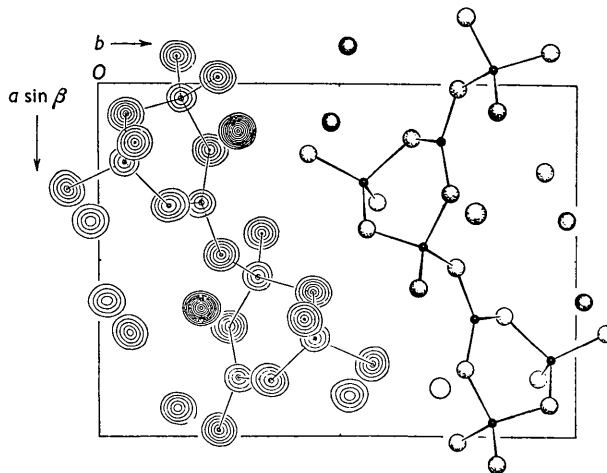


Fig. 2. Composite projection on (001) of the final electron-density sections for colemanite. Electron-density evaluated at intervals of $\frac{1}{5}$ in x, y, z . Boron atoms represented by small black circles, oxygen atoms by the smaller stippled circles, calcium atoms by the larger stippled circles, and water molecules by the line-shaded circles. The peaks for the oxygen and boron atoms are contoured at intervals of 5 e. \AA^{-3} , with the first contour at 5 e. \AA^{-3} ; the peak for the calcium atom is contoured at 10 e. \AA^{-3} , with the first contour at 10 e. \AA^{-3} .

the method of Schomaker & Shoemaker, as described above, and the corresponding atomic parameters are listed in column (5), Table 1.

The standard errors associated with the atomic parameters calculated from the least-squares analysis are listed in Table 2. The errors for the atoms of a given kind, i.e. for the eight oxygen atoms, or the three boron atoms, and for a given coordinate, i.e. for x, y or z , do not differ among themselves by more than 10^{-3} cycles. The standard error in \AA is about the same for the x - and y -parameters, for each kind of atom, but that for the z -parameter is larger in each case. As the z -parameters put into the least-squares refinement were relatively less precise and only one cycle of refinement was carried out, the results obtained are to be expected.

Table 5. *Calcium-oxygen and oxygen-oxygen interatomic distances in colemanite*

(See Figs. 3 and 4.)

Ca-O bonds. (All Ca-O bonds ± 0.02 Å)			
Ca-O ₂	2.42 Å	Ca-O ₁	2.51 Å
Ca-O ₃ *	2.43	Ca-O ₄	2.54
Ca-O ₆ *	2.41	Average = $\underline{2.52}$ Å	
Ca-O ₇ *	2.41		
Ca-O ₈ †	2.42		
Average = $\underline{2.42}$ Å			

O-O distances (oxygens bonded to same boron)

Triangle around B ₁			
O ₁ -O ₂	2.43 Å	O ₂ -O ₄	2.40 Å
O ₁ -O ₄	2.29		
Tetrahedron around B ₂			
O ₁ -O ₂	2.40 Å	O ₂ -O ₃ *	2.37 Å
O ₁ -O ₃ *	2.41	O ₂ -O ₅	2.42
O ₁ -O ₅	2.41	O ₃ -O ₅	2.43
Tetrahedron around B ₃			
O ₄ -O ₅	2.45 Å	O ₅ -O ₆ *	2.34 Å
O ₄ -O ₆ *	2.45	O ₅ -O ₇ *	2.48
O ₄ -O ₇ *	2.38	O ₆ *-O ₇ *	2.51

O-O distances (oxygens not bonded to same boron)

(Only distances < 3.0 Å listed; all O-O bonds ± 0.03 Å)

O ₁ -O ₆ *	2.80 Å	O ₅ -O ₇ *	2.73 Å
O ₂ -O ₃ *	2.98	O ₆ *-O ₈ †	2.88
O ₃ *-O ₅	2.74	O ₇ *-O ₈ †	2.76
O ₃ *-O ₆ *	2.90	O ₈ †-O ₈ †	2.73

* Hydroxyl groups.

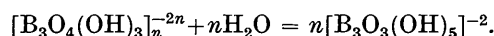
† Water molecule.

of orthoboric acid, H₃BO₃, where only triangularly coordinated boron occurs, Zachariasen (1954) found an average of 1.362 Å for the length of the B-OH bonds. In the monoclinic form of metaboric acid, HBO₂, the average B-O bond length is 1.36 Å for the triangularly coordinated boron and 1.46 Å for the tetrahedrally coordinated boron, on the basis of the semi-refined structure (Zachariasen, 1952). Morimoto (1956) has found in borax the average B-O bond lengths of 1.36 Å and 1.48 Å, respectively. Other instances in which both tetrahedrally and triangularly coordinated boron occur in the same polyion or chain have been reported in the literature. The B-O bond lengths given in these latter investigations, while in general agreement with those found by us, are probably not known as accurately as those we have quoted above. The bond angles, Ca-O bond lengths, and interatomic distances between oxygen atoms bonded to the same boron atom found in the present study all seem reasonable, and are in agreement with the corresponding values found by other investigators for borates.

It is difficult to decide whether the variation in the B-O bond lengths in the two tetrahedra of the ring element has real significance. Undoubtedly, the requirement that the lattice energy of the crystal be minimized results in packing effects that in turn bring

about bond length and bond angle variations. Just what variations would be expected is difficult to predict. In any event, the B-O bond lengths are not now known with sufficient accuracy to make further consideration of the bond length variation worthwhile.

The ring consisting of two boron-oxygen tetrahedra and a boron-oxygen triangle linked at corners is evidently a particularly stable configuration. Meyerhofferite (Christ & Clark, 1956), the synthetic compound 2 CaO.3 B₂O₃.9 H₂O (Clark & Christ, 1957), and inyoite (Clark, private communication) contain this unit as the isolated polyion [B₃O₃(OH)₅]⁻². The relationship between the infinite chains of colemanite and the polyions contained in meyerhofferite and the synthetic compound may be represented by the polymerization reaction:



It is stereochemically possible to add one BO₂(OH) triangle to the polyion [B₃O₃(OH)₅]⁻² to form the new polyion [B₄O₅(OH)₄]⁻², a polyion which has in fact recently been found in borax by Morimoto (1956). Drawings of the colemanite chains and the polyions found in meyerhofferite and in borax are shown in Fig. 5.

In Nature, colemanite and meyerhofferite are often found pseudomorphous after the highest hydrate of this series, inyoite, 2 CaO.3 B₂O₃.13 H₂O (Palache, Berman & Frondel, 1951). This observation is in agreement with the discovery by Clark that inyoite also contains the polyions [B₃O₃(OH)₅]⁻², and that the additional water exists in the crystal as water molecules so that the formula of inyoite may be written as CaB₃O₃(OH)₅.4 H₂O.

Electrical properties, symmetry, and hydrogen bonding

Pyroelectric polarity in colemanite has long been suspected by museum curators, who have observed that large crystals collect dust mainly along their edges, as though the crystals were electrically charged. Although the X-ray diffraction study leads to a non-polar structure in colemanite at room temperature, several workers have recently confirmed the presence of electrical activity. In a study of the patterns formed by electrical breakdown paths, Davisson (1956) concludes that colemanite shows the point-symmetry 2/m at 150 °C. and 30 °C., and perhaps also at -195 °C. He found, however, that colemanite is both pyroelectric and piezoelectric. His plot of the pyroelectric constant against temperature yields a curve that goes through a high and narrow peak (half-width 3°) at -2.5 °C., with an appreciable tail on the low temperature side and a small rapidly decreasing value for the constant on the high temperature side. He found the monoclinic *b*-axis to be the polar axis. When the structure was determined and reported in preliminary form in 1954, it was apparent that the presence of any

electrical activity must be due to structural phenomena involving a displacive transition in which the centrosymmetric structure found at room temperature becomes slightly distorted into a noncentrosymmetric state. Consequently it was suspected by us at an early stage that the crystal might be ferroelectric. The presence of ferroelectricity in colemanite was confirmed by Goldsmith (1956) who found colemanite to be ferroelectric below a transition temperature of -2.5°C ., with the monoclinic b -axis as the ferroelectric axis, and with indications that the ferroelectric phase remains monoclinic. He found the transition to be of the second order. Chynoweth (1957) has also measured the pyroelectric properties of colemanite and found a second order transition at -6°C . to a ferroelectric phase, the b -axis being the polar axis. He concludes, however, in disagreement with Davisson, that at temperatures higher than about -5°C ., an ideal single crystal of colemanite shows no pyroelectric effect and is centrosymmetric above this temperature.

In our own work we have found no indications of any departure from the space-group $P2_1/a$, even on greatly overexposed films. All of these results seem to indicate that any departure from centrosymmetry at room temperature is, in any event, small. This conclusion is in agreement with the recent findings of Holuj & Petch (1958). In a preliminary report on a nuclear magnetic resonance study of the boron sites in colemanite, they show that the room temperature spectra can be explained in detail on the basis of the point group $2/m$, whereas colemanite in the ferroelectric state appears to have the point group 2.

S. Block and G. Burley, of the U.S. National Bureau of Standards, (private communication), have examined the $h0l$ and $0kl$ nets of colemanite at room temperature and at temperatures below the Curie point. They find that when colemanite is in the ferroelectric phase, several diffraction spots appear on the film having $h = 2n+1$ for $h0l$ reflections. When the crystal is warmed through the transition temperature these spots disappear. There are no changes in the $0kl$ net at the higher and lower temperatures. These results together with the findings of Holuj & Petch (1958) indicate that colemanite has the space group $P2_1$ in the ferroelectric state.

The role of hydrogen atoms in the structure can only be inferred indirectly from the X-ray diffraction studies. It has been shown that only one oxygen atom (O_8) is present which is not bonded to a boron atom, and this atom must be identified as a water molecule. Thus, three hydrogen atoms remain to be associated with the oxygen atoms of the ring element. Of the seven oxygens in the B_3O_7 rings, four are linked to two boron atoms each, and therefore are nearly saturated with respect to their valency. These are O_1 , O_2 , O_4 and O_5 . The remaining three oxygen atoms, O_3 , O_6 and O_7 , are bonded to one boron each and evidently are hydroxyl groups. This arrangement of oxygens

bonded to two borons, and hydroxyl groups bonded to one boron has been found to occur in several borate polyions, and appears to be characteristic of this type of grouping.

Thus, in metaboric acid, $\text{H}_3\text{B}_3\text{O}_6$ (Zachariasen, 1954), three of the ring oxygen atoms are doubly linked and three singly linked; in meyerhofferite (Christ & Clark, 1956), in the ring $[\text{B}_3\text{O}_3(\text{OH})_6]^{-2}$, three oxygen atoms are doubly linked and five are singly linked; in borax (Morimoto, 1956), in the ring $[\text{B}_4\text{O}_5(\text{OH})_4]^{-2}$, five oxygen atoms are doubly linked and four are singly linked.

In colemanite, there are four interchain oxygen-oxygen distances between 2.73 and 2.76 Å, and three between 2.80 and 2.90 Å (see Table 5). These distances suggest the presence of a system of hydrogen bonds in the structure, some of which are normal, and others only partly occupied owing probably to some sort of disorder. These bonds can be traced through the structure in the manner shown in Fig. 3. O_5 is a linked oxygen which receives hydrogen bonds from the hydroxyl groups O_3 and O_7 of the neighboring chain, these bonds having lengths 2.74 Å and 2.73 Å, respectively. O_7 receives a normal hydrogen bond from the water molecule O_8 of length 2.76 Å. The two water molecules are separated by 2.73 Å and are presumably joined by a hydrogen bond, but since there is a center of symmetry in the structure lying midway between the two water molecules, it must be assumed that the polar hydrogen atom in the bond is contributed half the time by one molecule and half the time by the other (as, for example, in the ice structure). The water molecule lies at a distance of 2.88 Å from the hydroxyl group O_6 , which suggests that when the water molecule is not contributing a hydrogen atom to the water-water bond, it is directing a hydrogen bond toward O_6 . The hydroxyl group O_6 lies 2.80 Å from the linked oxygen O_1 and 2.90 Å from the hydroxyl group O_3 , suggesting that it directs a hydrogen bond toward these two atoms, each about half the time. In this way, all of the hydrogen atoms are accounted for, in full-time hydrogen bonds of average length 2.74 Å, and half-time hydrogen bonds of average length 2.87 Å. The terms 'full-time' and 'half-time' imply a disordered state, which, of course, may be either dynamic or static as far as the X-ray evidence is concerned.

The fact that colemanite is ferroelectric with a Curie temperature of -2.5 to -6°C . indicates that at room temperature the disorder in the hydrogen bonds is dynamic, and disappears below the transition point. At this point, the hydrogen bond between the water molecules probably becomes permanently polarized, thus destroying the center of symmetry. One of the two associated O_6 - O_8 spans would then become shortened to make a permanent hydrogen bond of normal length 2.75 Å, while the other O_6 - O_8 interatomic distance would presumably become a normal van der Waals contact of about 3.0 Å. The hydroxyl

O_6 may also become permanently bonded below the Curie temperature to either O_1 or O_3 . In any case, the space group symmetry through such an ordering of hydrogen bonds would be reduced either to Pa or $P2_1$, but no prediction as to which can be made at the present time on the basis of the structure determination alone. Just recently, it has been found experimentally that the transition to the ferroelectric state is accompanied by lowering of the symmetry from $P2_1/a$ to $P2_1$ (Holuj & Petch, 1958; Block & Burley, private communication). The symmetry operator a has the effect of determining the spatial relationship of each ring element in the colemanite chain to the succeeding element along the a -axis. It seems likely, then, that the transition involves an ordering of the hydrogen bonds in such a way as to destroy this constraint, with the creation of the resulting spontaneous polarization.

A neutron diffraction study of the hydrogen bonding in colemanite is certainly suggested by the results obtained here. The present authors have no plans to make such a study.

Comparison of signs determined from final structure with those calculated by Hauptman-Karle method

It is inherent in the statistical method that the signs of some of the structure factors be indeterminate, as well as that some seemingly well-determined signs be incorrect. In order to establish the determinancy of a sign some criterion or group of criteria must be set up. In the present investigation this was done by examining the way in which the signs and magnitudes of the contributions entered into the Σ_1 , Σ_2 , and Σ_3 formulas (Karle *et al.*, 1958) used for calculating the structure factor signs. The final set of structure factor signs was based on the results of applying the formulas Σ_{3i} , Σ'_{3i} , Σ''_{3i} (Karle *et al.*, 1958). The number of terms entering into a typical Σ_3 calculation was 300. It was decided to accept the sign of the structure factor as the sign of the corresponding sum if the magnitude of the sum exceeded $2(n)^{\frac{1}{2}}$ where n is the number of contributions, i.e. for 300 contributions where the magnitude of the sum exceeded 34. Two examples of the details of the calculations for typical Σ_3 's are given in Table 6. The first example, for the reflection (612), illustrates a case where the sign has a high probability of being negative; the second example, for the reflection (416), illustrates a case where the sign is indeterminate.

In the initial stages of the investigation the signs for 1997 reflections were calculated, out of the possible 2028 reflections observed, and of those calculated 188 signs were found to be indeterminate. After the refinement of the structure was completed the signs fixed by the accepted structure were compared with those calculated by the statistical method. It was found that of the 1809 determinate signs, 171, or 9.5% were

Table 6. Details of calculations of Σ'_{3i} for $h_i k_i l_i = 612$ and $h_i k_i l_i = 416$

$$\Sigma'_{3i} = \Sigma_{j < i} \mp \left[E_{h_j k_j l_j} \Sigma_{k_\mu} (-1)^{h_\mu + k_\mu} (E_{h_\mu k_\mu l_\mu}^2 - 1) \right] \begin{cases} k_j = k_i \\ h_\mu = \frac{1}{2}(h_i \pm h_j) \\ l_\mu = \frac{1}{2}(l_i \pm l_j) \end{cases}$$

$h_j k_j l_j$	$h_\mu l_\mu$	$E_{h_j k_j l_j}$	Σ_{k_μ}	$\mp E_{h_j k_j l_j} \Sigma_{k_\mu}$
(For $h_i k_i l_i = 612$)				
14,1,0	10,1	3.61	9.54	-34.44
	4,1		-8.18	-29.53
$\bar{1}\bar{2}$,1,2	3,2	3.37	4.14	-13.95
	9,0		-17.40	-58.65
2,1,2	4,2	3.05	20.40	-62.13
	2,0		10.41	-31.70
$\bar{8}$,1,10	1,6	-2.52	-12.72	-32.06
	7,4		4.48	-11.29
$\bar{8}$,1,6	1,4	-2.64	-5.38	-14.20
	7,2		8.13	-21.48
10,1,4	8,3	-2.64	-7.49	-19.81
	2,1		6.65	-17.58
0,1,10	3,6	-2.88	-9.79	-28.14
	3,4		5.18	-14.89
2,1,8	4,5	-2.94	-5.74	-16.85
	2,3		8.23	-24.15
6,1,6	6,4	-3.05	-10.19	-31.03
				$\Sigma'_{3i} = -461.88$

The sign of (612) is very probably negative.

$$\Sigma'_{3i} = -461.88$$

$h_j k_j l_j$	$h_\mu l_\mu$	$E_{h_j k_j l_j}$	Σ_{k_μ}	$\mp E_{h_j k_j l_j} \Sigma_{k_\mu}$
(For $h_i k_i l_i = 416$)				
14,1,0	9,3	3.61	19.03	-68.71
	5,3		0.22	0.80
$\bar{1}\bar{2}$,1,2	4,4	3.37	2.57	-8.66
	8,2		10.45	35.20
2,1,2	3,4	3.05	-0.32	0.97
	1,2		3.63	11.06
$\bar{8}$,1,10	2,8	-2.52	-7.20	-18.14
	6,2		-4.92	12.38
6,1,2	5,4	-2.60	3.36	8.74
	1,2		-3.67	9.53
$\bar{8}$,1,6	2,6	-2.64	-6.97	-18.42
	6,0		-2.33	6.16
10,1,4	7,5	-2.64	18.11	47.89
	3,1		-4.14	10.95
0,1,10	2,8	-2.88	-9.05	-26.04
	2,2		-2.24	6.44
2,1,8	3,7	-2.94	1.53	4.49
	1,1		9.95	-29.22
6,1,6	5,6	-3.05	3.13	9.54
				$\Sigma'_{3i} = -5.04$

The sign of (416) is indeterminate.

wrong. About one-third of those structure factors whose sign was wrong had one Miller index equal to zero. For the $h0l$ zone, of 93 possible reflections, 4 were indeterminate, and 4 were wrong. A relatively large number of incorrect signs were obtained, therefore, for the $0kl$ and $hkl0$ zones. We have not attempted an analysis of these results for the zones. In all cases where the sign was incorrect there was no correlation between this fact and the magnitude of the Σ_3 , or the magnitude of the E_{hkl} or F_{hkl} .

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Structure du Cyanure de Sodium Hydraté

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$\text{NaCN} \cdot 2 \text{H}_2\text{O}$ crystallizes in the monoclinic system. The space group is $P2_1/a$. The unit-cell dimensions are: $a = 6.54$, $b = 10.66$, $c = 6.08$ Å, $\beta = 103^\circ$, with four molecules per unit cell. The crystal structure has been determined by direct sign-determining methods and by means of electron-density projections on the (001) and (010) planes. An indication of the position of the hydrogen atoms was obtained from ($\rho_\sigma - \rho_c$) maps. All the atoms are in general positions. Each sodium atom is surrounded by a group of four oxygen atoms and two $(\text{CN})^-$ ions. The $\text{C}\equiv\text{N}$ bond length is 1.07 Å and the $\text{Na}-(\text{CN})$ distance: 3 Å. The nitrogen atom is bonded to an oxygen atom by hydrogen bond; the $\text{N} \cdots \text{O}$ distance is 2.81 Å.

Introduction

Les cristaux que nous avons utilisés pour nos expériences ont été préparés, à température ordinaire, par évaporation lente d'une solution aqueuse de cyanure de sodium. Ils correspondent à la formule $\text{NaCN} \cdot 2\text{H}_2\text{O}$. Leur symétrie est monoclinique.

Paramètres et groupe d'espace

Les paramètres de la maille ont été mesurés sur des clichés de cristal tournant, effectués avec la radiation $\text{Cu } K\alpha$ ($\lambda = 1,541$ Å). L'angle β a été obtenu sur le cliché de Weissenberg $h0l$. Les résultats sont les suivants:

$$a = 6,54 \pm 0,01, \quad b = 10,66 \pm 0,01, \quad c = 6,08 \pm 0,01 \text{ \AA}, \\ \beta = 103^\circ \pm 30', \quad Z = 4.$$

$$\text{Densité mesurée: } 1,361 \text{ g.cm.}^{-3}. \\ \text{Densité calculée: } 1,368 \text{ g.cm.}^{-3}.$$

Les extinctions systématiques observées sur les diagrammes de Weissenberg sont:

$$\text{réflexions } h0l \text{ éteintes pour } h = 2n+1, \\ \text{réflexions } 0k0 \text{ éteintes pour } k = 2n+1.$$

Ce système d'extinctions conduit sans ambiguïté au groupe centrosymétrique $P2_1/a-C_{2h}^5$.