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Hauptman-Karle phase determination applied to meyerhofferite *

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With 1 figure

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Auszug

Das Verfahren zur Bestimmung der Strukturfaktorvorzeichen für den in der Raumgruppe $P\bar{1}$ kristallisierenden Meyerhofferit, $CaB_3O_3(OH)_5 \cdot H_2O$ wird ausführlich dargelegt. Unter Verwendung der Σ_1-, Σ_2- und Σ_3-Beziehungen nach Hauptman und Karle (1953) war es möglich, 2303 unter insgesamt 2678 Vorzeichen, für die $|F_{hkl}|_{\text{beob.}} > 0$, routinemäßig zu bestimmen. Von den 2303 Vorzeichen erwiesen sich auf Grund der endgültigen Daten der Strukturbestimmung nur 55 als falsch.

Abstract

The procedures used to calculate the signs of the structure factors for meyerhofferite, $CaB_3O_3(OH)_5 \cdot H_2O$, a $P\bar{1}$ crystal, are described in detail. Using the Σ_1, Σ_2, and Σ_3 relationships of Hauptman and Karle, Monograph I (1953), it was possible to determine routinely 2303 signs out of a possible 2678 for which $|F_{\mathrm{h}}(\text{obs.})| > 0$. Of the 2303 determinate signs only 55 were wrong as judged by the final structure.

Introduction

When the investigation of the crystal structure of meyerhofferite, $CaB_3O_3(OH)_5 \cdot H_2O$, was begun, no application of the Hauptman-Karle phase-determination procedures (Hauptman and Karle, 1953; hereafter referred to as Monograph I) had yet been made to a $P\bar{1}$ crystal of unknown structure. The crystal structure of colemanite, $CaB_3O_4(OH)_3 \cdot H_2O$, in space group $P2_1/a$ (Christ, Clark and Evans, 1954, 1958) had readily yielded to the Hauptman-Karle method (Karle, Hauptman and Christ, 1958), but doubt had been expressed

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as to whether the method could be successful for a crystal in space group $P\bar{1}$ (VAND and PEPINSKY, 1954). However, the signs of the structure factors for meyerhofferite were readily calculated and the structure determined (CHRIST and CLARK, 1956, preliminary account). Subsequent to the solutions of the crystal structures of colemanite and meyerhofferite the structures of the more complex crystals *p,p'*-dimethoxybenzophenone, $CH_3OC_6H_4COC_6H_4OCH_3$, (KARLE, HAUPTMAN, KARLE and WING, 1957, 1958), and spurrite, $Ca_4(SiO_4)_2CO_3$, (HAUPTMAN, KARLE, KARLE and SMITH, 1959) have been solved by these statistical procedures.

The present paper is a detailed account of the procedures used and the results obtained in the application of the method of Hauptman and Karle to meyerhofferite. The crystal structure of meyerhofferite is described in an accompanying paper (CHRIST and CLARK, 1960).

Preliminary considerations

Normalized structure factors E_h

The three-dimensional intensity data collected for meyerhofferite (CHRIST and CLARK, 1960) were corrected for Lorentz and polarization factors to obtain the F_{h}^2(obs.). For meyerhofferite, there are 4342 independent reflections contained in the reciprocal sphere of radius $s = (\sin\theta)/\lambda = 0.9$ Å^{-1}; of this number 2678 were observed to have intensities greater than zero, 1515 had intensities below the threshold of observation and were assigned zero values and no observations were made on the remaining 149, all of which have $s \geq 0.8$ Å^{-1}. The calculation of the phases was based therefore on 4193 intensity observations.

The F_{h}(obs.) were put on an absolute scale and corrected for the vibrational motion of the atoms through the use of the $K(s)$ function described by KARLE and HAUPTMAN (1953). The $K(s)$ curve for meyerhofferite, shown in Fig. 1, was obtained in the following way. A listing was made, in order of increasing s, of the quantities F_{h}^2(obs.) and

$$\sigma_2 = \sum_{j=1}^{N} f_j^2(s)$$

(where N is the total number of atoms in the unit cell and f_j is the scattering factor of the jth atom). For meyerhofferite the cell contents are $2[CaB_3O_3(OH)_5 \cdot H_2O]$. The s range was divided into ten intervals containing nearly equal numbers of terms, about 430. The $K(s)$ value for each of these s intervals was calculated by means of the relation

$$K(s) = \frac{\Sigma \sigma_2}{\Sigma F_{\mathrm{h}}^2 (\mathrm{obs.})},$$

where the summations extend over each s interval, and $K(s)$ is plotted against the midpoint of the interval. For the ten groups containing nearly equal numbers of terms the values represented by the solid circles in Fig. 1 were obtained. The same procedure was also carried out using s intervals for which the first interval contained 155 terms, and nine remaining intervals each contained about 460 terms. The values obtained in this latter calculation are plotted as crosses in Fig. 1. Finally, the smooth monotonically increasing curve $K(s)$ was drawn among these points. The value of $[K(0)]^{1/2}$, the factor for converting the $|F_{\mathrm{h}}(\mathrm{obs.})|$ to an absolute scale, is 2.82. The corresponding scale factor found by least-squares comparison of the $|F_{\mathrm{h}}(\mathrm{obs.})|$ and the structure factors calculated from the final atomic parameters has the concordant value of 2.86 (Christ and Clark, 1960).

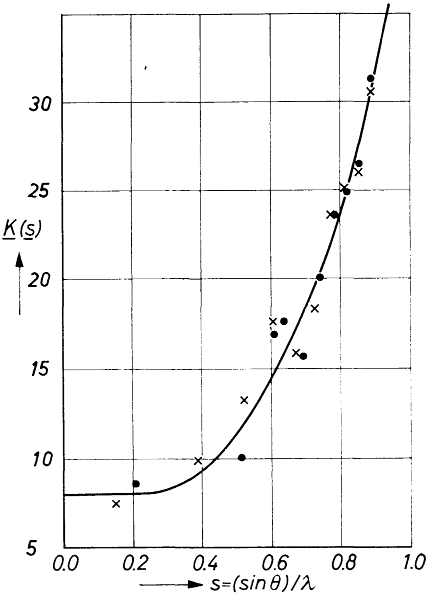

Fig. 1. $K(s)$ curve for meyerhofferite. Solid circles show positions of averages when each group contains an approximately equal number of terms; crosses show positions of averages obtained when the first s interval contains 155 terms and each of the remaining intervals contains 460 terms

The quantities E_{h}^2, where $|E_{\mathrm{h}}|$ is defined as the normalized structure factor, were computed according to equation 3.15, Monograph I:

$$E_{\mathrm{h}}^2 = \frac{nK(s) F_{\mathrm{h}}^2 (\mathrm{obs.})}{m_2 \sigma_2}.$$

For the space group $P\bar{1}$, the symmetry number n, and the mixed moment m_2, are both equal to 2 (Monograph I pp. 44–45).

According to Karle *et al.* (1958), the probability distribution of a structure factor in a centrosymmetric crystal predicts $32^0/_0$ of all $|E| > 1$, $5^0/_0$ of all $|E| > 2$, and $0.3^0/_0$ of all $|E| > 3$. For meyerhofferite the actual distribution found is as follows: $34^0/_0$ with $|E| > 1$, 4.4% with $|E| > 2$, and 0.2% with $|E| > 3$. Similarly, the theoretical averages expected for a centrosymmetric crystal are: $<|E|> = 0.798$, $<E^2> = 1.0$, and $<|E^2-1|> = 0.968$. The values found are 0.715, 0.986, and 1.01, respectively. The deviations are principally due to the fact that the intensities of the absent reflections were taken as zero.

Arrangement of data

For ease in carrying out the sign-determining procedures the data were divided into eight groups according to whether h,k,l ($\equiv \mathbf{h}$) are odd or even integers. The symbol g (for *gerade*) is used for an even integer and the symbol u (for *ungerade*) for an odd integer. Thus, the eight possible groups are: *ggg, ggu, guu, uuu, ugg, uug, ugu,* and *gug.* For each group two listings were made. In the first of these listings $F_{\mathbf{h}}^2$(obs.), $E_{\mathbf{h}}^2$, $E_{\mathbf{h}}^2-1$, and $|E_{\mathbf{h}}|$ were recorded in dictionary order on *hkl*; in the second, these same data were recorded in order of decreasing $|E_{\mathbf{h}}|$. In Table 1 are shown for each group the total number of terms, the number of terms for which $|E_{\mathbf{h}}| > 0$, and the largest $|E_{\mathbf{h}}|$.

Table 1. *Grouping of meyerhofferite data according to* $|E_{\mathbf{h}}|$ *values*

$\mathbf{h}$	No. of terms	No. of terms, $\|E_{\mathbf{h}}\| > 0$	Largest $\|E_{\mathbf{h}}\|$	$\mathbf{h}$ for largest $\|E_{\mathbf{h}}\|$
ggg	539	317	3.07	$\bar{2}.12.6$
uuu	548	369	3.21	$\bar{9}\bar{3}9$
guu	539	344	3.62	$\overline{10}.1.7$
ugu	549	355	3.85	$\bar{9}29$
uug	540	326	3.02	11.5.0
ggu	539	344	2.93	$\bar{8}.10.3$
gug	539	323	3.49	$\overline{10}.\bar{1}.2$
ugg	549	300	2.83	$7\bar{8}0$

Sign determination

Initial procedure

The calculation of signs by the Hauptman-Karle procedure must begin with the determination of at least some of the signs of the *ggg* group. Two probability relationships are available initially, namely those given by equations 3.29 and 3.32, Monograph I. Only the Σ_1 relationship given by the first of these equations was used in the present study. For the $P\bar{1}$ case, this may be written (KARLE *et al.*, 1958) as

$$P_+(F_{2\mathbf{h}}) = \tfrac{1}{2} + (\text{coefficient})\,|E_{2\mathbf{h}}|(E_{\mathbf{h}}^2-1),$$

where the coefficient is

$$\frac{\sum_{j=1}^{N} Z_j^3}{4\left(\sum_{j=1}^{N} Z_j^2\right)^{3/2}},$$

and for meyerhofferite has the numerical value of 0.067. For a crystal with N equal atoms the coefficient above reduces to $1/(4N^{1/2})$. Setting $1/(4N^{1/2}) = 0.067$, we calculate $N \simeq 14$. Hence a $P\bar{1}$ crystal with seven equal atoms in the asymmetric unit would yield the same coefficient as that given by the thirteen unequal atoms of meyerhofferite*.

Thus the heavier calcium atom helps in the initial sign determination. However, as is discussed later in this paper, the presence of the calcium atom in an otherwise essentially equal-atom structure causes errors in the overall sign determination. $P_+(2\mathbf{h})$ was evaluated for each of the *ggg* terms of meyerhofferite. This procedure is quite rapid using the listings described above, and for most of the terms involved can be done by inspection. Eight terms were found to have $P_+(2\mathbf{h}) > 0.80$, seven with $P_+(2\mathbf{h})$ lying between 0.7 and 0.8, and two with reasonably strong probabilities of having negative signs, giving a total of seventeen terms, the signs of which have high probabilities. Data for the eight strongly positive terms and the two negative terms are given in Table 2. The sign calculated by $P_+(F_{2\mathbf{h}})$, by the complete statistical procedure, and from the final structure is the same for each of these ten terms, except for $2\mathbf{h} = 8\bar{4}4$, where $P_+(F_{2\mathbf{h}})$ yielded the wrong answer.

The signs of the first eight terms of Table 2 were checked for internal consistency through the use of the Σ_3 relationship given by equation 4.05, Monograph I, which may be written (Karle *et al.*, 1958) as

$$sE_{2\mathbf{h}} \sim s\sum_{\mathbf{k}} E_{2\mathbf{k}}(E^2_{\mathbf{h}+\mathbf{k}} - 1).$$

In this equation s stands for 'sign of' and $\sim$ indicates 'probably is'. For the Σ_3 calculation any one term of the eight may be taken as the $2\mathbf{h}$ term and each of the remaining seven terms plus their centrosymmetric equivalents as the $2\mathbf{k}$ terms, making a total of fourteen possible contributors to Σ_3. Sample calculations are given in Tables 3 and 4.

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* The contribution of the hydrogen atoms to the numerical value of the coefficient is negligible.

Table 2. *Some ggg terms with high probabilities calculated using the* Σ_1 *relationship* $P_+(F_{2\mathbf{h}}) = \frac{1}{2} + 0.067\,|E_{2\mathbf{h}}|\,(E_{\mathbf{h}}{}^2 - 1)$

2h	$\lvert E_{2\mathbf{h}}\rvert$	$\lvert F_{2\mathbf{h}}\rvert$	$P_+(F_{2\mathbf{h}})$	Final sign, H-K method	Final sign, structure
$\bar{2}.12.6$	3.07	6.0	1.00*	+	+
10.6.2	1.66	3.1	1.00*	+	+
080	2.16	10.4	0.94	+	+
$\overline{10}.4.6$	2.16	4.2	0.89	+	+
$8\bar{4}4$	2.17	5.0	0.88	—	—
$\bar{2}.\overline{12}.6$	1.20	2.4	0.83	+	+
$\bar{6}\bar{6}2$	1.08	4.1	0.83	+	+
284	1.55	5.4	0.82	+	+
$\bar{4}.0.10$	2.42	5.7	0.34	—	—
$\bar{2}.\overline{12}.4$	2.56	6.1	0.36	—	—

* Calculated greater than 1.00 due to series termination errors.

Table 3. *Calculation of the sign of* $E_{10.6.2}$ *using the* Σ_3 *relationship* $sE_{2\mathbf{h}} \sim s\underset{\mathbf{k}}{\Sigma} E_{2\mathbf{h}}\,(E^2_{\mathbf{h}+\mathbf{k}} - 1)$

2h = 10.6.2 $\lvert E_{2\mathbf{h}}\rvert = 1.66$

2k	$E_{2\mathbf{k}}$	h + k	$E^2_{\mathbf{h}+\mathbf{k}} - 1$	$E_{2\mathbf{k}}\,(E^2_{\mathbf{h}+\mathbf{k}} - 1)$
$\bar{2}.12.6$	3.07	494	2.89	8.86
$2.\overline{12}.\bar{6}$	3.07	$6\bar{3}\bar{2}$	0.58	1.78
$8\bar{4}4$	2.17*	913	− 1.00	− 2.17
$\bar{8}4\bar{4}$	2.17*	$15\bar{1}$	0.91	1.97
080	2.16	571	0.16	0.35
$0\bar{8}0$	2.16	$5\bar{1}1$	0.22	0.48
$\overline{10}.4.6$	2.16	054	2.35	5.07
$10.\bar{4}.\bar{6}$	2.16	$10.1.\bar{2}$	11.17	24.09
284	1.55	673	1.62	2.50
$\bar{2}8\bar{4}$	1.55	$4\bar{1}\bar{1}$	2.12	3.27
$\bar{2}.\overline{12}.6$	1.20	$4\bar{3}4$	2.42	2.91
$2.12.\bar{6}$	1.20	$69\bar{2}$	1.36	1.64
$\bar{6}\bar{6}2$	1.08	202	2.16	2.32
$66\bar{2}$	1.08	860	2.39	2.57
				$\Sigma_3 = 55.64$

* Assumed + from $P_+(F_{2\mathbf{h}})$; actually —.

The statistical criterion for the acceptance or rejection of a sign was to require that Σ_3 be greater than three standard deviations, *i.e.* $\Sigma_3 > 3n^{1/2}$, where n is the number of contributors to Σ_3. This criterion was later strengthened for terms with $|E| < 1.00$ to require that $|E|\ \Sigma > 3n^{1/2}$, where Σ is any one of the sums Σ_1, Σ_2, or Σ_3 used throughout the work. The calculation shown in Table 3 has $\Sigma_3 = 55.6 \gg$

Table 4. *Calculation of the sign of* $E_{8\bar{4}4}$ *using the* Σ_3 *relationship* $sE_{2\mathrm{k}}\, s\sum\limits_{\mathrm{k}} E_{2\mathrm{k}} \sim (E^2_{\mathrm{h+k}} - 1)$

$2\mathrm{h} = 8\bar{4}4$ $|E_{2\mathrm{h}}| = 2.17$

2k	$E_{2\mathrm{k}}$	h + k	$E^2_{\mathrm{h+k}} - 1$	$E_{2\mathrm{k}}(E^2_{\mathrm{h+k}} - 1)$
$\bar{2}.12.6$	3.07	345	−0.52	−1.61
$2.\overline{12}.\bar{6}$	3.07	$5\bar{8}\bar{1}$	−0.08	−0.25
080	2.16	422	−0.95	−2.04
$0\bar{8}0$	2.16	$4\bar{6}2$	−0.44	−0.95
$\overline{10}.4.6$	2.16	$\bar{1}05$	−1.00	−2.16
$10.\bar{4}.\bar{6}$	2.16	$9\bar{4}\bar{1}$	0.18	0.39
10.6.2	1.66	913	−1.00	−1.66
$\overline{10}.\bar{6}.\bar{2}$	1.66	$\bar{1}\bar{5}1$	0.91	1.51
284	1.55	524	−0.81	−1.25
$\bar{2}\bar{8}\bar{4}$	1.55	$3\bar{6}0$	−0.26	−0.41
$\bar{2}.\overline{12}.6$	1.20	$3\bar{8}5$	0.24	0.29
$2.12.\bar{6}$	1.20	$54\bar{1}$	−0.62	−0.74
$\bar{6}\bar{6}2$	1.08	$1\bar{5}3$	−0.08	−0.09
$66\bar{2}$	1.08	711	−0.79	−0.85
				$\Sigma_3 = -9.82$

$3(14)^{1/2} = 11$, so that the sign of $E_{10.6.2}$ is acceptable as positive, whereas the results shown in Table 4 yield $\Sigma_3 = -9.8 < 3(14)^{1/2} = 11$ so that the sign of $E_{8\bar{4}4}$ is indeterminate. The Σ_3 check also showed the sign of E_{080} to be indeterminate. Thus of the eight original $E_{2\mathrm{h}}$ having high sign probabilities, six remained as a nucleus for further calculation of E_{ggg} signs by Σ_3. The next eight E_{ggg} with large $P_+(F_{2\mathrm{h}})$ were then examined and seven of these met the statistical acceptance criterion. The total of thirteen E_{ggg} having high sign probabilities were then used for Σ_3 calculation of the signs of the E_{ggg} having large $|E|$. The first thirty of such terms were examined in order of decreasing $|E|$, and signs were accepted for twenty-two of these. Further reiteration of the internal consistency checks eliminated one of the original thirteen terms. In this manner was assembled a group of thirty-four E_{ggg} with known signs, composed of twenty-two of the first thirty terms in order of decreasing $|E|$ and twelve of the seventeen terms having large $P_+(F_{2\mathrm{h}})$. This group was then used for digital computer calculation of the Σ_3 for all E_{ggg}. At the end of this procedure it was considered that about two-thirds of the signs for the *ggg* group were determined. Some large $|E|_{ggg}$ still had indeterminate signs and an effort was made to fix these using the Σ_2 relationship of equation 4.04, Monograph I. The sign of only one of the $E_{2\mathrm{h}}$ could be determined by the use of Σ_2 at this stage of the calculations.

Intermediate and final stages

At the completion of the inital stage only signs for the *ggg* group were determined. In order to start sign determination for the $E_{\mathbf{h}}$ of the remaining seven groups it was first necessary to fix the origin of the $P\bar{1}$ cell by the arbitrary assignment of signs to three $E_{\mathbf{h}}$ where the three $\mathbf{h}$ are linearly independent modulo 2 (Monograph I). The $E_{\mathbf{h}}$ having the largest magnitudes are usually chosen for sign assignment, because this practice leads to strong probability results in the determination of new signs. Of the remaining seven groups, *ugu* and *guu* contain the two largest $|E_{\mathbf{h}}|$ values (Table 1). Accordingly, the two terms, $E_{\bar{9}29} = 3.85$ and $E_{\overline{10}.\bar{1}.7} = 3.62$, were taken as positive. Of the five remaining groups, only the signs of the E_{uug} are fixed by the choice made above. The choice of the third sign can therefore be made for an $E_{\mathbf{h}}$ from among the groups *uuu, ggu, gug,* or *ugg*. In these groups, $E_{gug} = E_{\overline{10}.1.2.} = 3.49$ is the largest (Table 1); its sign was taken as positive. The origin is thus determined and the signs of all of the remaining $E_{\mathbf{h}}$ are fixed by the crystal structure.

The computation of the signs of the E_{ugu} was carried out using Σ_2, which can be written as $sE_{\mathbf{h}} \sim s\sum_{\mathbf{k}} E_{\mathbf{k}}E_{\mathbf{h}+\mathbf{k}}$ (KARLE *et al.*, 1958). The calculation necessarily started with $E_{\mathbf{k}} = E_{\bar{9}29} = +3.85$, (since $E_{\bar{9}29}$ has the only known sign of the *ugu* group), taken together with some of the $E_{\mathbf{h}+\mathbf{k}} = E_{ggg}$ with previously determined signs. The procedure actually followed was to calculate the product $E_{\bar{9}29}E_{ggg}$ for the E_{ggg} of largest magnitudes, and then to accept the signs only for those $E_{\mathbf{h}}$ of large magnitude. This process is equivalent to evaluating $P_+(F_{\mathbf{h}})$, which for Σ_2 is proportional to $|E_{\mathbf{h}}|E_{\mathbf{k}}E_{\mathbf{h}+\mathbf{k}}$. In this way the signs of eight additional E_{ugu} of large magnitude were obtained. The internal consistency of the set of nine E_{ugu} was checked using Σ_2, with completely satisfactory results. This nucleus of nine E_{ugu} with known signs was then used in hand calculation of Σ_2 to derive the signs of 21 additional E_{ugu} of large magnitude. In turn, the collection of 30 E_{ugu} of known signs was used in digital computer calculation to derive the signs of the remaining E_{ugu}. Although a knowledge of the signs of 30 $E_{ugu} = E_{\mathbf{k}}$ permits a possible total of 60 contributors to $\underset{\mathbf{k}}{\Sigma_2}$, in practice the number of contributors is limited by lack of information about the appropriate $E_{\mathbf{h}+\mathbf{k}} = E_{ggg}$. The actual number of contributors for meyerhofferite was usually about 14, with the largest number noted being 30, and the smallest, 1. At the conclusion of the digital computer calculations it was judged from the statistical criteria that $65^0/_0$ of the signs of the E_{ugu} were determined.

Analogous procedures were followed for the calculation of the signs of the E_{guu}, starting with $E_{\overline{10}.1.7} = +\,3.62$, and the E_{gug}, starting with $E_{\overline{10}.\overline{1}.2} = +\,3.49$. At the end of these calculations it was considered that 75% of the signs of the E_{guu}, and 85% of the signs of the E_{gug} were determined.

At this stage there remained the calculation of the signs of the $E_{\mathbf{h}}$ for the four groups *uug*, *ggu*, *ugg*, and *uuu*. These signs are dependent on the signs already determined. For example, in using $\underset{\mathbf{k}}{\Sigma_2}$ for the *uuu* group the indices take the form $\mathbf{h} = uuu$, $\mathbf{k} = gug$, and $\mathbf{h} + \mathbf{k} = ugu$. As the signs of some of these four dependent groups become known various combinations can be used in Σ_2 for cross-checking. As an example the set *gug* can be obtained from the combinations $ugg + uug$, $ggu + guu$, and $ugu + uuu$, (in addition to the $ggg + gug$ already used). In the present study, the signs of the E_{uuu} were calculated next. A list of 50 E_{gug} of large magnitude and known sign were used as the $E_{\mathbf{k}}$ of $\underset{\mathbf{k}}{\Sigma_2}$ in combination with the $E_{\mathbf{h}+\mathbf{k}} = E_{ugu}$ of known sign. The signs for the remaining groups *uug*, *ggu*, and *ugg* were then calculated in a similar way. After the completion of these computations, the signs of the E_{ggg} were recalculated using $\underset{\mathbf{k}}{\Sigma_2}$ with $\mathbf{k} = uug$ $(\mathbf{h} + \mathbf{k} = u'u'g')$, and the signs of the E_{ugu} recalculated with $\mathbf{k} = gug$ $(\mathbf{h} + \mathbf{k} = uuu)$. The recalculations increased the percentage of determinate signs to 86% for each of these two groups. At this stage the overall percentage of determinate signs was likewise 86%; statistics for the distribution of the determinate signs among the several groups are given in Table 5.

Discussion of results

After the crystal structure of meyerhofferite was refined by least-squares analysis (CHRIST and CLARK, 1960), the signs determined by the structure were compared term by term with those calculated by the Hauptman-Karle procedures. It was found that 97.5% of the signs determined by the statistical procedure are correct. A detailed listing of some of the results of the comparison of signs is given in Table 5.

Errors in sign determination are known to be caused by the presence in a crystal structure of unequal atoms, as well as by the finite number of data available. For several non-centrosymmetric space-groups, equations have been given by KARLE and HAUPTMAN (1956) for calculating the variance to be expected. Similar statistical considera-

Table 5. *Summary of results for Hauptman-Karle sign determination*

Group	(1) No. of terms with $\|F_h(\text{obs.})\| > 0$	(2) No. of deter-minate signs*	(3) No. of deter-minate signs wrong**	(4) No. of terms with $\|E_h\| \geqq 1.0$	(5) No. of deter-minate signs, $\|E_h\| \geqq 1.0$*	(6) No. of deter-minate signs wrong $\|E_h\| \geqq 1.0$**
ggg	317	275	5	185	179	3
ugu	355	306	8	174	170	3
guu	344	261	7	180	165	2
gug	323	277	4	187	177	2
uuu	369	337	11	170	163	4
ggu	344	299	7	184	182	5
uug	326	297	10	180	172	4
ugg	300	251	3	170	166	2
Total	2678	2303	55	1430	1374	25

* Signs judged determinate by the statistical criteria, $\Sigma > 3n^{1/2}$ where n is the number of contributors to Σ, for all $|E_h| \geq 1.0$; for $|E_h| < 1.0$, $|E_h|\ \Sigma > 3n^{1/2}$.

** Final signs on basis of crystal structure (CHRIST and CLARK, 1960).

Table 6. *Some signs incorrectly determined by Hauptman-Karle procedures*

h	$\|E_h\|$	Σ_2 (final)	$\|F_h(\text{obs.})\|$*	$F_h(\text{calc.})$**	ΔF
$1\bar{4}1$	3.49	16.66	35.4	− 33.1	− 2.3
$\bar{2}\bar{2}2$	2.62	− 26.20	26.6	23.1	3.4
$\bar{1}12$	2.30	72.02	23.4	− 22.7	− 0.7
$0\bar{1}1$	2.06	23.42	20.9	− 22.4	1.5
$0\bar{5}2$	2.03	− 25.82	20.6	20.7	− 0.1
111	1.93	− 57.35	19.6	15.9	3.7
$\bar{4}\bar{4}5$	1.83	− 22.72	18.5	20.4	− 1.9
$0\bar{2}1$	1.79	− 99.69	18.2	16.6	1.6
$2\bar{1}3$	1.78	− 17.46	18.0	15.4	2.6
$\bar{2}03$	1.75	− 22.61	17.8	14.7	3.1

* Value includes the final scaling factor, $k = 2.86$.

** F_k(calc.) from final positional and thermal parameters for meyerhofferite (CHRIST and CLARK, 1960).

tions are associated with Σ_2 in centrosymmetric space-groups. The variance calculated for meyerhofferite indicates that about $3^0/_0$ of the determinate signs with $|E| > 1.0$ will be wrong as a result of the presence of the calcium atom in an otherwise equal-atom structure (H. HAUPTMAN, oral communication). This result is in good agreement with the result found experimentally. About half of the incorrect signs were for terms with $|E| > 1.0$, and for about one-third of the incorrect signs at least one of the corresponding Miller indices was zero. A similar situation was found for colemanite (CHRIST, CLARK, and EVANS, 1958). Some detailed information on ten large E_{h} for which the procedure led to incorrect signs is given in Table 6. In some of these cases a large Σ_2 is evidently associated with an incorrect sign.

Since the sign determination for meyerhofferite was completed, an algebraic approach to the phase-determination problem has produced new and important relationships for use in centrosymmetric and non-centrosymmetric crystals (HAUPTMAN and KARLE, 1957; KARLE and HAUPTMAN, 1958). However, we wish to emphasize that from the practical standpoint the joint-probability method of Hauptman and Karle was very effective when used in this manner. The systematic application of the several Σ equations to successive groups of reflections is easy to carry out, and the power of the method due to the cumulative effect produced by systematic reiteration is evident in the successful determination of the meyerhofferite phases.

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