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Crystal Structure of Spurrite, $Ca_5(SiO_4)_2CO_3$. I. Determination by the Probability Method

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The direct determination of the phases from the experimental X-ray intensities of spurrite has been carried out by means of the probability method. The structure of spurrite was thereby deduced. This crystal is of particular interest since it illustrates the relationship between rational dependence and renormalization. Owing to the approximate rational dependence of several atoms and the limited number of experimental data, it afforded the opportunity to apply the renormalization procedure.

1. Introduction

The mineral, spurrite, crystallizes in space group $P2_1/a$ with four stoichiometric units per unit cell. Using about one half of the Cu sphere, 1172 independent reflections, obtained from Dr J. V. Smith, the structure was deduced by means of the probability methods described in Monograph I (Hauptman & Karle, 1953), which yield the phases of the structure factors directly from the observed intensities. Examination of the averages of $E^2_{\mathbf{h}}$ over certain subsets of reciprocal space showed that they differed significantly from unity, indicating that the crystal contained a substantial amount of rational dependence. It was therefore necessary to employ a renormalization procedure suggested in Chapter 5 of Monograph I (1953) and developed further in a recent paper (Hauptman & Karle, 1959). The present paper contains an outline of the procedure for phase determination and illustrates the usefulness of renormalization.

2. Renormalization

An examination of the listing of the $E^2_{\mathbf{h}}$ for spurrite revealed several subsets whose averages differed significantly from unity. These are listed in Table 1 together with the standard deviations of the averages. The need for renormalization is apparent.

Table 1

Averages of E^2 (column 2) over subsets for spurrite showing the need for renormalization. The third column shows the number of elements in each subset while the fourth column gives the standard deviations of the means appearing in column 2. Column 5 gives calculated averages arising from the presence of the rationally dependent atoms whose positions are given by the idealized coordinates of Table 3. In column 1, g signifies even and u odd

Subsets	$\langle E^2\rangle$	n	$(2/n)^{\frac{1}{2}}$	$\langle E^2_i\rangle$
$g0l,\ h+l \equiv 0 \pmod 3$	1·672	42	0·22	2·351
$g0l,\ h+l \not\equiv 0 \pmod 3$	0·682	85	0·15	0·861
$ggl,\ h+l \equiv 0 \pmod 3$	2·462	81	0·16	4·338
$ggl,\ h+l \not\equiv 0 \pmod 3$	1·216	160	0·11	1·358
$uul,\ h+l \equiv 0 \pmod 3$	1·531	97	0·14	1·386
$uul,\ h+l \not\equiv 0 \pmod 3$	0·758	192	0·10	0·619
$h \not\equiv k \pmod 2$	0·710	517	0·06	0·374
All data	1·008	1174	0·04	1·000

In preparing the listing of the data, we form the renormalized $(E^2_{\mathbf{h}}-\overline{E^2})$ (Hauptman & Karle, 1959) instead of the usual $(E^2_{\mathbf{h}}-1)$, where $\overline{E^2}$ is the appropriate average of the subset to which $E^2_{\mathbf{h}}$ belongs, found from column 2 of Table 1. In deriving the $E^2_{\mathbf{h}}$ from the observed intensities by the usual statistical means, it is assumed that

$$\langle E^2_{\mathbf{h}}\rangle_{\mathbf{h}} = 1\ , \qquad (2{\cdot}1)$$

where the average is taken over all vectors included in the sphere of reflection. It should be noted that, in spite of the rational dependence, this assumption remains essentially correct.

3. Phase determination

The following phase determining formulas were used:

$$\Sigma_1:\qquad sE_{2h\,0\,2l} \sim s\sum_{k}(-1)^{h+k}(E^2_{hkl}-\overline{E^2})\ , \qquad (3{\cdot}1)$$

$$sE_{0\,2k\,0} \sim s\sum_{h,l}(-1)^{h+k}(E^2_{hkl}-\overline{E^2})\ , \qquad (3{\cdot}2)$$

$$\Sigma_2:\qquad sE_{\mathbf{h}} \sim s\sum_{\mathbf{k}} E_{\mathbf{k}}E_{\mathbf{h}+\mathbf{k}}\ , \qquad (3{\cdot}3)$$

and

$$\Sigma_3:\qquad sE_{\mathbf{h}} \sim s\sum_{\mathbf{k}} E_{\mathbf{k}}(E^2_{(\mathbf{h}+\mathbf{k})/2}-\overline{E^2})\ , \qquad (3{\cdot}4)$$

where s means ‘sign of’ and the symbol $\sim$ means ‘probably is’.*

The relation (3·1) is used to start the phase determination. Table 2 illustrates the application of (3·1) to the largest E_{2h02l}. It is seen that Σ_1 without renormalization is much less definitive for the $E_{\bar{8}08}$ and the E_{204} than the Σ_1 with renormalization. It turns

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* Other useful forms of Σ_3 for space group $P2_1/a$ may be found in a previous publication (Karle, Hauptman & Christ, 1958). In these formulas $\overline{E^2}$ replaces 1.

out that, with the number of data available for this structure determination, it was not possible to build up a sufficiently broad base of signs on which to carry through the phase determination, unless the structure factors were renormalized.

Table 2

Values of Σ_1 for the four largest E_{g0g}. Comparison of columns 3 and 4 shows the improvement resulting from the renormalization. Column 5 gives the number of contributors to Σ_1 while column 6 is the standard deviation of the sum Σ_1.

$2h,0,2l$	E	Σ_1 with renormalization	Σ_1 without renormalization	n	$(2n)^{\frac{1}{2}}$
$\bar{8}08$	−2·45	−8·03	−2·59	7	3·74
$\bar{6},0,12$	+2·19	+6·69	+9·51	6	3·45
$\bar{8}02$	+2·15	+8·97	+15·17	7	3·74
204	−2·11	−2·99	−0·17	6	3·45

The contribution of Σ_1 with renormalization as seen in Table 2 is definitive for the four E_{2h02l} listed. This may be determined by referring to the last column in which the standard deviation of the sum, Σ_1, appears. It should be noted that the measure of reliability in standard deviations is somewhat greater than the magnitude of the ratio of columns 3 to 6. This is due to the fact that the computed value for Σ_1 is not to be compared with zero, but with the correct value for Σ_1. Hence the true measure of the probability that Σ_1 will give the incorrect sign for the corresponding E is obtained by multiplying the ratio of columns 3 to 6 by a factor of the order of 1·5 to 2.

The negative sign indication of Σ_1 for E_{204}, which is somewhat weaker than the others in Table 2, is readily confirmed by means of Σ_2 using, for example, $E_{\bar{8}08}$ and $E_{\bar{6}012}$. The continued application of Σ_1, Σ_2 and Σ_3 led to the determination of the signs of 204 of the biggest $E_{\mathbf{h}}$ from which two and three-dimensional Fourier maps were computed. Two of the phases were incorrectly determined.

4. Results

The (010) and (100) projections, made with the initially determined set of signs are shown in Figs. 1(*a*), (*b*), respectively. The series computed with F_o for the (010) projection had 39 terms and that for the (100) projection had 28 terms. One sign for the (010) projection was subsequently shown to be incorrect. The calcium atoms are marked with an X in the diagrams, and the SiO_4 and CO_3 groups are indicated by lines connecting the Si–O bonds of the silicate tetrahedron and the C–O bonds of the carbonate triangle. Except for the appearance of the CO_3 group in the (010) projection the features of the structure are fairly well depicted in these initial maps. The three-dimensional map computed with E's facilitated the structure interpretation. Projections of the structure on the (010) and (100) planes, using all the observed $h0l$ and $0kl$ data and

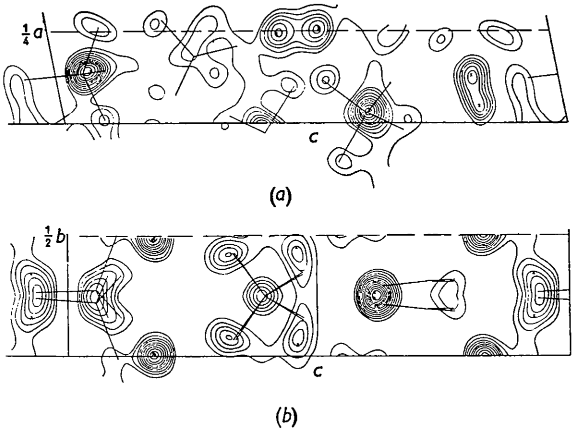

Fig. 1. (*a*) The (010) projection computed with 39 terms. (*b*) The (100) projection computed with 28 terms. Calcium atoms are marked with an X and Si–O and C–O bonds are indicated.

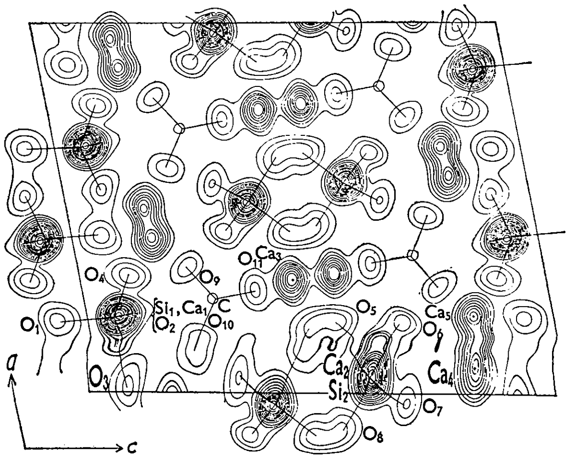

Fig. 2. The final (010) projection. Calcium atoms are marked with an X and Si–O and C–O bonds are indicated.

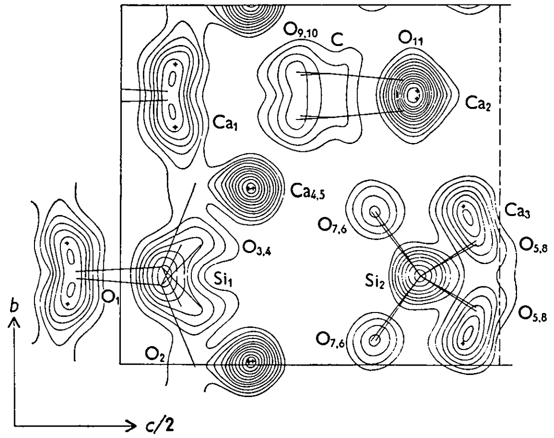

Fig. 3. The final (100) projection. Calcium atoms are marked with an X and Si–O and C–O bonds are indicated.

the signs from the refined structure, are illustrated in Figs. 2 and 3, respectively. A detailed description of the refined structure and its relation to that of other minerals will be given in the paper to follow (Smith, Karle, Hauptman & Karle, 1960).

5. Discussion

Once the structure of spurrite was known, it was of interest to discover the rationally dependent atoms giving rise to the averages appearing in column 2 of Table 1. The main features of the rational dependence are accounted for by the six atoms listed in Table 3.

Table 3

Coordinates of six atoms showing approximate rational dependence. These coordinates are idealized in columns 5–7 in order to clarify the nature of the rational dependence. Here $x=0{\cdot}134$ and $z=0{\cdot}068$

	Coordinates			Idealized coordinates		
Atom	x_j	y_j	z_j	x_j	y_j	z_j
Ca_1	0·140	0·662	0·072	x	$\frac{3}{4}$	z
Ca_2	0·467	0·740	0·388	$x+\frac{1}{3}$	$\frac{3}{4}$	$z+\frac{1}{3}$
Ca_4	0·455	0·490	0·169	$x+\frac{1}{3}$	$\frac{1}{2}$	$z+\frac{1}{12}$
Ca_5	0·133	0·507	0·826	x	$\frac{1}{2}$	$z+\frac{3}{4}$
Si_1	0·134	0·222	0·055	x	$\frac{1}{4}$	z
Si_2	0·475	0·249	0·396	$x+\frac{1}{3}$	$\frac{1}{4}$	$z+\frac{1}{3}$

Comparison of columns 2–4 with columns 5–7 respectively shows that these atoms are approximately rationally dependent. Idealized averages $\langle E_i^2 \rangle$ which would arise from the presence of atoms having the coordinates given in columns 5–7 of Table 3 were computed by the algebraic methods employed in a previous paper (Hauptman & Karle, 1959) and are listed in column 5 of Table 1. These are to be compared with the experimentally determined averages given in column 2 of Table 1. It is seen that they are in qualitative agreement. Aside from experimental and sampling errors, the main reason for the discrepancy between columns 2 and 5 of Table 1 is the fact that column 5 has been computed on the basis of idealized coordinates. In fact, it is important to note that since the rational dependence is only approximate, the averages $\langle E^2 \rangle$ listed in column 2 of Table 1 will approach unity as the number of experimental data increases. Thus the need for renormalization in this case would decrease as the number of available data became more extensive. It is clear that the renormalization compensates somewhat for the limited number of data which are experimentally available.

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