APPENDIX VI

Derivation of formula (72)

Let the integration of the left hand side of equation (72) be denoted by Q_n,

$$Q_n=\int_0^\infty 2\,E^{p+1}\exp(-E^2)\,R_{n,n}(E)\,dE\,. \quad \text{(VI-1)}$$

Substituting the polynomial

$$R_{n,n}(E)=(-1)^n n!L_n^{(p)}(E^2) \quad \text{(VI-2)}$$

into (VI-1), and then putting $E^2=x$, Q_n is rewritten

$$Q_n=(-1)^n\,n!\int_0^\infty e^{-x}x^{p/2}L_n^{(p)}(x)\,dx\,, \quad \text{(VI-3)}$$

where $L_n^{(p)}(x)$ is the Laguerre polynomial $L_n(x)$.

In order to carry out the integration of (VI-3), it is convenient to make use of the generating function of $L_n(x)$; namely,

$$\sum_{n=0}^\infty L_n(x)\,t^n=\frac{1}{(1-t)}\exp\left(-\frac{xt}{1-t}\right). \quad \text{(VI-4)}$$

Then, it follows from (VI-3) and (VI-4) that

$$\sum_{n=0}^\infty Q_n(-t)^n/n!=\int_0^\infty \exp\left(-\frac{x}{1-t}\right)x^{p/2}\frac{dx}{(1-t)}$$

$$=(1-t)^{p/2}\int_0^\infty e^{-X}X^{p/2}dX, \quad \text{(VI-5)}$$

where

$$\frac{x}{(1-t)}=X\,.$$

With the use of the well known relation

$$\int_0^\infty e^{-X}X^{p/2}dX=\Gamma\left(\frac{p+2}{2}\right), \quad \text{(VI-6)}$$

we obtain

$$\sum_{n=0}^\infty Q_n(-t)^n/n!=\Gamma\left(\frac{p+2}{2}\right)(1-t)^{p/2}\,. \quad \text{(VI-7)}$$

Comparison of the coefficients of the terms t^n on both sides of equation (VI-7) gives

$$Q_n=\Gamma\left(\frac{p+2}{2}\right)n!\binom{p/2}{n}$$

$$=\Gamma\left(\frac{p+2}{2}\right)\frac{p(p-2)(p-4)\ldots[p-(2n-2)]}{2^n}. \quad \text{(VI-8)}$$

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Application of a System of Linear Structure-Factor Equations to the Structure Determination of $LiB(OH)_4$*

By L. Kutschabsky and E. Höhne

Institut für Strukturforschung der Deutschen Akademie der Wissenschaften zu Berlin, Berlin-Adlershof, Germany

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If the atomic parameters are known in two dimensions, it is possible to determine the atomic parameters in the third direction with the help of a system (or systems) of linear structure-factor equations. The method has been used to determine the approximate structure of $LiB(OH)_4$.

Introduction

Ott (1927) and Avrami (1938) proposed a method for the direct determination of atomic parameters from the observed $F_{obs}(hkl)$ by means of a non-linear system of equations. This method has hitherto not been applied.

Assuming a knowledge of the atomic parameters in one projection (*e.g.* x_j, y_j), the determination of the third atomic parameters (z_j) is possible with the help of a system of linear structure-factor equations if the structure factors of one particular higher level of the reciprocal lattice [$F(hkL)$ with L constant] are used (Kutschabsky, 1965).

Theory

We shall limit our consideration to centrosymmetric structures. For the space group $P\bar{1}$ the following structure-factor equations hold (x_j, y_j known; L=const.):

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* Forming part of the doctorate thesis of L. Kutschabsky.

$$F_{\mathrm{obs}}(hkL)=\sum_{j=1}^{N}2\,.\,f_j\,.\,\cos 2\pi(hx_j+ky_j)\,.\,\cos 2\pi Lz_j$$
$$-\sum_{j=1}^{N}2\,.\,f_j\,.\,\sin 2\pi(hx_j+ky_j)\,.\,\sin 2\pi Lz_j\,. \quad (1)$$

We number the structure factors $F_{\mathrm{obs}}(hkL)$ to be used:

$F_{\mathrm{obs}}(hkL)=F_m^{(L)}$
($m=1,2,\cdots M$; $M=$ total number of equations).

We denote the known coefficients by

$$a_{mj}=2\,.\,f_j\,.\,\cos 2\pi(hx_j+ky_j)\,,\qquad b_{mj}=2\,.\,f_j\,.\,\sin 2\pi(hx_j+ky_j)$$

and the unknown transcendent variables by

$$C_j^{(L)}=\cos 2\pi Lz_j\,,\quad S_j^{(L)}=\sin 2\pi Lz_j\,.$$

Equation (1) may then be written in the form

$$F_m^{(L)}=\sum_{j=1}^{N}a_{mj}\,.\,C_j^{(L)}-\sum_{j=1}^{N}b_{mj}\,.\,S_j^{(L)}\,. \quad (2)$$

If we have no knowledge of the signs of the $F_{\mathrm{obs}}(hkL)$ the unobserved structure factors may be used to obtain a system of homogeneous linear equations. If there are $2N$ unknown variables $C_j^{(L)}$ and $S_j^{(L)}$, $M=2N-1$ independent homogeneous linear equations are necessary to determine a solution uniquely, *i.e.* to obtain the variables as functions of only one of them. It is of advantage to use, in addition to the homogeneous equations, one equation belonging to a strong structure factor whose sign may be fixed arbitrarily. This system of, now $2N$ equations gives approximations to the true values of $C_j^{(L)}$ and $S_j^{(L)}$ directly.

As the coefficients of these equations are inaccurate and, moreover, the structure factors are only approximately zero, the solution of $2N$ linear equations would give rather inaccurate values. Approximately correct values can be obtained by using a 'redundancy' of equations and minimizing the sum $\sum_{m=1}^{M}\delta_m^2$ of the squares of the deviations ($\delta_m=$ value of the left side minus value of the right side of the equation; see equation (6) below).

The $C_j^{(L)}$ and $S_j^{(L)}$ may be used to determine the signs of further structure factors. Taking these equations in addition to the other, the number of equations increases and therefore the accuracy of $C_j^{(L)}$ and $S_j^{(L)}$ will be improved. By computing several cycles most of the signs may be determined.

If the $F_{\mathrm{obs}}(hkL)$ are on an absolute scale, then the $C_j^{(L)}$ and $S_j^{(L)}$ are also absolute. The relation between the variables $C_j^{(L)}$ and $S_j^{(L)}$ makes it possible to determine the atomic parameters z_j of all atoms resolved in the (x,y) projection, if the structure factors $F(hkL)$ with $L=1$ are used.

The accuracy of the values z_j improves with increasing L. Therefore it is possible to refine the values of z_j by analogous computations for a higher level. Ambiguities may be avoided by considering the results of the first level.

If there are maxima (q) in the (x,y) projection which do not correspond to real atoms, the system of equations will give small values for the corresponding $C_q^{(L)}$ and $S_q^{(L)}$ for all levels. Therefore $(C_q^{(L)})^2+(S_q^{(L)})^2$ will be significantly smaller than for those corresponding to real atoms. This makes it possible to distinguish maxima corresponding to atoms from other maxima.

Application to the structure determination of $LiB(OH)_4$

Crystal data

Space group *Pbca*;

$$a=9{\cdot}16\,,\quad b=7{\cdot}95\,,\quad c=8{\cdot}54\ \text{Å}$$
$$Z=8\,.$$

The attempt to obtain the approximate structure from two-dimensional $M_4(x,z)$ minimum-functions taking oxygen–oxygen vectors across the centre of symmetry (in projection) as shift-vectors led to considerable difficulties. The minimum functions thus obtained could not be refined by two-dimensional Fourier synthesis. As we recognized later, all these minimum functions included correct maxima in addition to maxima which did not correspond to atoms. In this structure even one incorrect atom might change an appreciable number of signs. On the other hand we obtained the three-dimensional principle of the structure directly by using a system of linear equations. A detailed discussion of the stereochemical aspects will be published shortly.

Determination of the approximate structure

For the application of the system of equations it is necessary first to determine the position of the centre of symmetry in space. In the (x,z) projection there are two possibilities:

Case 1: Centre of symmetry in A' and screw axes in B'.

Case 2: The other way round (Fig. 1).

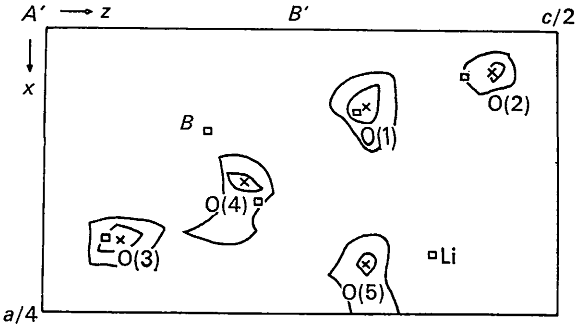

Fig. 1. Minimum function $M_4(x, z)$ for $LiB(OH)_4$ with points, marked with crosses, used as basis for the systems of linear equations and points, marked with squares, which result as atomic positions after refinement.

Case 1: $\bar{1}$ in A' $\quad 2_1$ in B'
Case 2: 2_1 in A' $\quad \bar{1}$ in B'

To start with, we considered both cases in parallel. The maxima in the $M_4(x,z)$ (Fig. 1) were assigned to oxygen atoms. From the formula for structure factors in *Pbca*

$$\begin{aligned} F_m^{l=2n+1}&(h1l) \\ &= \sum_{j=1}^{N} \{-4f_j \,.\, [1+(-1)^h] \,.\, \sin 2\pi h x_j \cdot \sin 2\pi l z_j \\ &\quad +4f_j \,.\, [1-(-1)^h] \cdot \cos 2\pi h x_j \,.\, \cos 2\pi l z_j\} \,.\, \cos 2\pi y_j \end{aligned}$$

in which h, l are short for h_m, l_m and

$$\begin{aligned} F_p^{l=2n}&(h1l) \\ &= \sum_{j=1}^{N} \{-4f_j \,.\, [1+(-1)^h] \,.\, \sin 2\pi h x_j \cdot \cos 2\pi l z_j \\ &\quad -4f_j \,.\, [1-(-1)^h] \cdot \cos 2\pi h x_j \,.\, \sin 2\pi l z_j\} \,.\, \sin 2\pi y_j \end{aligned} \qquad (3)$$

in which h, l are short for h_p, l_p, the coefficients follow:

$$\begin{aligned} a_{mj} &= -4f_j \,.\, [1+(-1)^h] \,.\, \sin 2\pi h x_j \,.\, \sin 2\pi l z_j \\ &\quad +4f_j \,.\, [1-(-1)^h] \,.\, \cos 2\pi h x_j \,.\, \cos 2\pi l z_j \\ b_{pj} &= -4f_j \,.\, [1+(-1)^h] \,.\, \sin 2\pi h x_j \,.\, \cos 2\pi l z_j \\ &\quad -4f_j \,.\, [1-(-1)^h] \,.\, \cos 2\pi h x_j \,.\, \sin 2\pi l z_j \,. \end{aligned} \qquad (4)$$

The parameters x_j, z_j of some of the atoms were known from the $M_4(x,z)$. With the help of the equations we determined the corresponding y_j (of the correct case) using the structure factors $F(h1l)$.

Two inhomogeneous systems of equations were obtained, consisting of the equations corresponding to the unobserved structure factors and of one equation each corresponding to a strong structure factor:

$$\begin{aligned} \sum_{j=1}^{N} a_{mj} \,.\, C_j^{(1)} &= F_m^{l=2n+1}(h1l) \\ &\quad (F_m^{l=2n+1}(h1l)=0 \text{ for } m=1,2,\ldots M-1 \\ &\quad F_m^{l=2n+1}(h1l) \neq 0 \text{ for } m=M; \\ &\quad C_j^{(1)}=\cos 2\pi y_j) \\ \sum_{j=1}^{N} b_{pj} \,.\, S_j^{(1)} &= F_p^{l=2n}(h1l) \\ &\quad (F_p^{l=2n}(h1l)=0 \text{ for } p=1,2,\ldots N-1 \\ &\quad F_p^{l=2n}(h1l) \neq 0 \text{ for } p=P; \\ &\quad S_j^{(1)}=\sin 2\pi y_j) \end{aligned} \qquad (5)$$

The solutions gave sets of values $C_j^{(1)}$ and $S_j^{(1)}$ in both cases. These sets satisfy the systems of equations only approximately and the sum of the squares of deviations $\Sigma\delta_m^2$, $\Sigma\delta_p^2$, respectively

$$\begin{aligned} \delta_m &= |F_m(h1l)| - |\sum_{j=1}^{N} a_{mj} \,.\, C_j^{(1)}| \\ \delta_p &= |F_p(h1l)| - |\sum_{j=1}^{N} b_{pj} \,.\, S_j^{(1)}| \,, \end{aligned} \qquad (6)$$

could therefore be used as a criterion to find out which of the two cases is realized. We found that case 1 is correct. By means of $(C_j^{(1)})^2+(S_j^{(1)})^2$ we could then decide which of the maxima of the $M_4(x,z)$ (Fig. 1) correspond to atoms. These are the atoms O(1) $\cdots$ O(4). Maximum O(5) does not correspond to an atom. By means of formula (3), using the approximate values $C_j^{(1)}$ and $S_j^{(1)}$, a considerable number of the signs of the structure factors could be determined. From the system of equations with a now stronger 'redundancy', more accurate values $C_j^{(1)}$ and $S_j^{(1)}$ could be obtained. Even the retaining of the 'incorrect atom' had only a small influence on the values of $C_j^{(1)}$ and $S_j^{(1)}$ $(j=1\ldots4)$ of the correct atoms, because the $C_5^{(1)}$ and $S_5^{(1)}$ belonging to the 'incorrect atom' are small. After three cycles we obtained the results shown in Table 1.

Table 1. *Values of* $C_j^{(1)}$ *and* $S_j^{(1)}$ *after three cycles*

$C_1^{(1)} = 0{\cdot}687$	$S_1^{(1)} = 0{\cdot}337$
$C_2^{(1)} = -0{\cdot}441$	$S_2^{(1)} = -0{\cdot}863$
$C_3^{(1)} = 0{\cdot}754$	$S_3^{(1)} = 0{\cdot}592$
$C_4^{(1)} = -0{\cdot}407$	$S_4^{(1)} = 1{\cdot}000$
$C_5^{(1)} = 0{\cdot}159$	$S_5^{(1)} = 0{\cdot}115$

The first four pairs of values in Table 1 correspond to oxygen atoms. In comparing the values y_j computed from $C_j^{(1)}$ and $S_j^{(1)}$ with the values obtained after three-dimensional refinement ($R=0{\cdot}07$) (Table 2), we have to keep in mind that the parameters x_j and z_j used for computing the coefficients a_{mj} and b_{pj} were not very accurate, as they were obtained from a minimum function without refinement.

Table 2. *Comparison of* y_j *from* $C_j^{(1)}$ *and* $S_j^{(1)}$ *with values of* y_j *obtained after three-dimensional refinement*

	y_j from $C_j^{(1)}$ and $S_j^{(1)}$	y_j after refinement
O(1)	0·09	0·0665
O(2)	0·68	0·7050
O(3)	0·10	0·0760
O(4)	0·32	0·3353

Atomic parameters after three-dimensional refinement are recorded in Table 3.

Table 3. *Atomic parameters for* $LiB(OH)_4$

Atom	*x*	*y*	*z*
O(1)	0·0753	0·0665	0·3099
O(2)	0·0468	0·7050	0·4151
O(3)	0·1889	0·0760	0·0591
O(4)	0·1540	0·3353	0·2083
B	0·0925	0·1708	0·1652
Li	0·1986	0·8690	0·3752
H(1)	0·0246	0·1600	0·3860
H(2)	0·0875	0·5850	0·4250
H(3)	0·2430	0·4750	0·1100
H(4)	0·0806	0·4200	0·2250

Application of the method to structures with weak layers in the reciprocal lattice

The structure of $Ca(BO_2)_2 \,.\, 4H_2O$ (soon to be published) is an example of such a structure. The $F(hkl)$ with

$l=2n+1$ are weak, because there are pairs of calcium atoms nearly coinciding in (x,y) projection and differing in their z parameters by $\frac{1}{2}$. Therefore it was not possible to determine the signs of $F(hkl)$ $(l=2n+1)$ by calculating the contributions of the calcium atoms. But by using a system of linear equations, the signs of these $F(hkl)$ were obtained directly and also the z_j parameters of the oxygen atoms, which had been found without difficulty in the (x,y) projection.

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Structure et Mécanisme de Croissance du Gypse

PAR B. SIMON ET M. BIENFAIT
Laboratoire de Minéralogie et Cristallographie de l'Université de Nancy, France

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The theory of crystal growth by deposition of growth units in equivalent steps (Kossel, Stranski, Volmer, Frank) is applied to gypsum. This proposed mechanism is interesting even in such a complex structure. The periodic bond chain theory based upon the assumption of the forces between nearest neighbours only, allows the possible growth layers and the structure of the growth unit to be found easily. A few thermodynamical quantities, which are relevant to crystal growth, are calculated. A theoretical habit of gypsum can be then derived; the agreement with the observed habit is not particularly good, and this is shown to be the consequence of the adsorption of the solvent on faces and edges of the crystal.

1. Introduction

Le mécanisme de croissance d'un cristal est compris dans son principe depuis les études de base de Kossel (1927), Stranski (1928), Volmer (1939) et Frank (Burton, Cabrera & Frank, 1951). Pour les faces stables du cristal, le trait fondamental est la croissance périodique, rangée après rangée, couche après couche, par incorporation d'unités de croissance dans les sites de pas répétable (wiederholbarer Schritt). Les deux schémas de la Fig. 1 rappellent ces séquences fondamentales dans le cas d'une germination bidimensionnelle et dans le cas de l'avancement d'un gradin d'une dislocation à composante vis. Ces schémas simples ont peu touché les cristallographes car l'application de la théorie a la réputation d'être peu efficace quand il s'agit d'une structure autre que cubique simple, cubique centrée, c.f.c., ou hexagonale compacte. Pourtant la généralité de ce modèle ne doit faire aucun doute. Notre but ici est de montrer que l'établissement d'un tel modèle de croissance pour un cristal de complexité moyenne (gypse), ainsi que les calculs énergétiques que cela exige, ne rencontrent aucune difficulté de principe pour le cristallographe.

Nous allons procéder en deux temps. Au paragraphe 2, en nous appuyant sur la méthode des P.B.C. de Hartman & Perdok (Hartman, 1953; Hartman & Perdok, 1955), nous rechercherons les séquences cristallographiques possibles de la croissance: rangées de croissance (P.B.C.) et couches de croissance (tranches des faces *F*).

Ces résultats purement qualitatifs seront précisés et corrigés au paragraphe 3, où nous effectuons les calculs énergétiques qui nous permettront d'établir définitivement pour le gypse les mécanismes de croissance généralisés de Kossel, Stranski, Volmer, Frank.

2. Étude géométrique

Dans la théorie de Hartman & Perdok (1955), la connaissance des chaînes périodiques de liaisons entre atomes (P.B.C.) permet de trouver les faces qui croissent par couches de croissance, c'est à dire par le mécanisme décrit en 1 (faces *F*). Certaines conditions doivent être réalisées (Hartman, 1963):

(i) Une couche de croissance a une épaisseur minimum d_{hkl} correspondant à la symétrie de position du cristal.
(ii) Elle contient au moins deux P.B.C. non parallèles.
(iii) Elle n'a pas de moment dipolaire qui lui soit perpendiculaire.

On procède par approximations successives, en cherchant d'abord par des considérations simples les directions des P.B.C.

2·1. *Détermination des directions des P.B.C. du gypse dans l'hypothèse des liaisons entre premiers voisins*

La structure du gypse (Wooster, 1936; Pake, 1948) est constituée de doubles feuillets SO_4Ca parallèles à (010), unis entre eux par des molécules d'eau. Dans un premier examen de cette structure à l'aide d'un modèle la matérialisant, on considère les liaisons entre