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A Tangent Formula Derived from Patterson-Function Arguments. IV. The Solution of Difference Structures Directly from Superstructure Reflections

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Abstract

The possibility of solving by direct methods the difference structure δ of a superstructure using only the intensities of the superstructure reflections $\mathbf{h}$ is shown. The refinement of the phases Φ of the strong superstructure E values, which are normalized separately from the E values of the main or substructure reflections, is carried out maximizing the function $Z_{\delta P'} = \sum_{\mathbf{h}}(E_{\mathbf{h}} - \langle E_{\mathbf{h}}\rangle)C_{\mathbf{h}}(\Phi)$, where $C_{\mathbf{h}}(\Phi)$ is the amplitude of the structure factor of δ^3 expressed in terms of Φ. The maximization is performed with a new tangent formula that only differs from that given previously [Rius (1993). *Acta Cryst.* A**49**, 406–409] by an extra summation, *i.e.* the phase information is now derived from quartets and negative quintets instead of triplets and negative quartets. A preliminary test calculation demonstrates the capability of this tangent formula to solve the difference structure of the mineral wermlandite using only the measured superstructure intensities. Although more tests covering a variety of situations are still required to allow for a generalization, this result seems to confirm the viability of determining the internal structure of reconstructed surfaces by interpreting the corresponding three-dimensional difference Patterson function by direct methods. Access to this function is now possible, since, with the advent of intense synchrotron sources, not only in-plane intensity data but also the corresponding diffraction rods can be measured.

1. Introduction

1.1. *'Klassengleiche' superstructures – some basic concepts and definitions*

A superstructure is a structure that can be regarded as a complication of a simpler one. This simpler or average structure $\overline{\rho}$ is obtained by averaging the electron density over all n subcells of the supercell (or over all asymmetrical units) (Buerger, 1959) (Fig. 1) and contains per volume unit n times more symmetry operations than the superstructure, *i.e.*, according to the theory of groups, the space group of the superstructure is a subgroup of index n of the space group of the average structure. If the subgroup is maximal and if the reduction of symmetry operations affects the number of lattice points, the resulting superstructure is called *klassengleich* (Hermann, 1929). The reduction of lattice points causes the appearance of superstructure reflections ($\mathbf{h}$), which are systematically weaker than the main reflections ($\mathbf{H}$). The different mean intensity of the two reflection sets is due to the different amounts of electron density that contribute to each set. This can be best illustrated with the one-dimensional superstructure in Fig. 1(*a*) consisting of two heavy atoms with form factors f_P placed at the origin of the 'subcells' (at $x = 0, 1/2$) and of two lighter atoms with form factors f_L at $x = \pm x_L$. The structure-factor expression for the main (m) and superstructure (s) reflections are, respectively,

$$F_m(H) = 2f_P + 2f_L\cos(2\pi Hx_L)$$

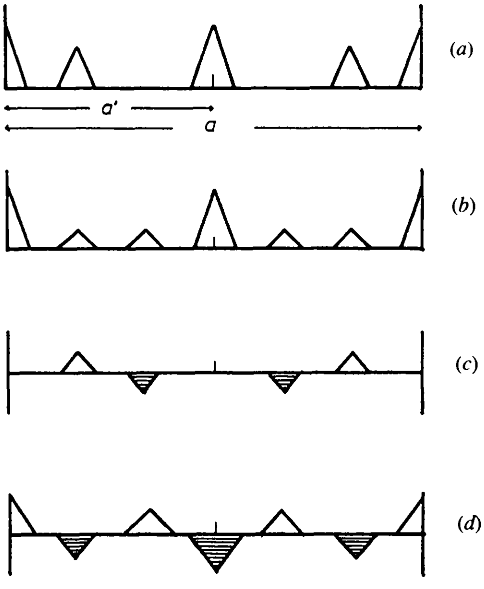

Fig. 1. (*a*) $\rho(\mathbf{x})$ = one-dimensional superstructure of replacive type ($n = 2$); (*b*) $\overline{\rho}(\mathbf{x})$ = average structure; (*c*) $\delta(\mathbf{x})$ = difference structure; (*d*) $\delta P(\mathbf{u})$ = difference Patterson.

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and

$$F_s(h) = 2f_L\cos(2\pi hx_L),$$

i.e. the h reflections are systematically weaker because the heavy atoms only contribute to the main reflections.

The difference structure δ (Fig. 1) is defined as the difference between the superstructure and the average structure (Takéuchi, 1972), *i.e.*

$$\delta(\mathbf{x}) = \rho(\mathbf{x}) - \bar{\rho}(\mathbf{x}). \tag{1}$$

The difference structure δ has the same symmetry as the superstructure but, in contrast to the average structure, has positive and negative values. Depending on what happens to a given site when passing from the space group of the average structure to the subgroup of the superstructure, different peak distributions will be obtained in δ. Three cases may be distinguished.

(*a*) The site symmetry is reduced, the multiplicity is maintained and, consequently, the site can gain additional degrees of freedom. In this way, one atom can shift from its ideal position, giving rise to an antisymmetric peak in δ. If most peaks in δ are antisymmetric, the superstructure is of *displacive* type (Fig. 2). Fig. 3 shows the shape of the antisymmetric peaks for different shifts t. Inspection of this figure gives the conclusion (Allmann & Rius, 1985) that, for small shifts ($t \leq 1\sigma$ Å): (i) the separation s between the maximum and the minimum of the peak is almost constant ($\cong 2\sigma$ Å); and (ii) the height of the maximum of the peak decreases with decreasing t. This result was confirmed by analyzing the triclinic superstructure of $Na_{10}(H_2W_{12}O_{42})\cdot 27H_2O$ (Rius, 1980; Allmann & Rius, 1985). In this compound, the averaged shift $\langle t\rangle$ for the 12 W atoms is 0.14 Å, while the found separation is 1.0 Å, *i.e.* much greater than the observed shift.

(*b*) The site symmetry is preserved when the site separates and different atom types can occupy the resulting sites. This produces separate positive and negative peaks in δ and the corresponding superstructures are called of *replacive* type (Fig. 1).

(*c*) A decomposition of the site in different parts is also possible, *e.g.* one part maintains the symmetry while the other increases the number of degrees of freedom. This produces antisymmetric as well as separated positive and negative peaks in the corresponding δ. In any case, the site decomposition must satisfy the equation

$$n = p\sum_{j=1}^{t} p_j^{-1}, \tag{2}$$

where n is the index of the subgroup, p is the order of the site-symmetry group before symmetry reduction and t is the number of resulting site types with orders p_j after symmetry reduction.

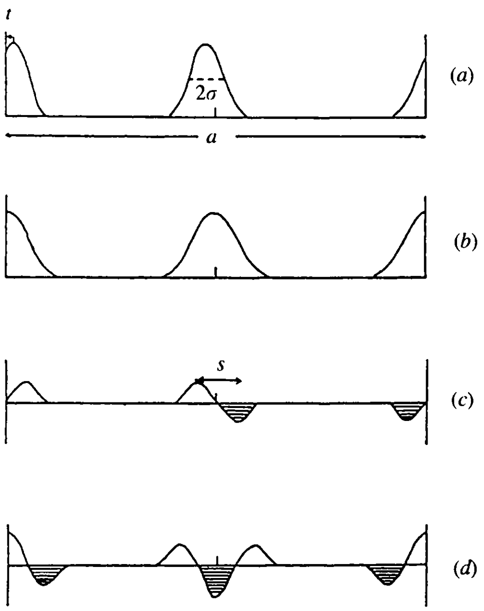

Fig. 2. (*a*) $\rho(\mathbf{x})$ = one-dimensional superstructure of displacive type ($n = 2$) built of Gaussian 'atomic' peaks with standard deviation σ; (*b*) $\bar{\rho}(\mathbf{x})$ = average structure; (*c*) $\delta(\mathbf{x})$ = difference structure; (*d*) $\delta P(\mathbf{u})$ = difference Patterson. t is the atomic shift from the ideal position and s is the maximum-to-minimum separation in the antisymmetric peaks (for $t < \sigma$, $s = 2\sigma$; for $t > \sigma$, $s \cong 2t$).

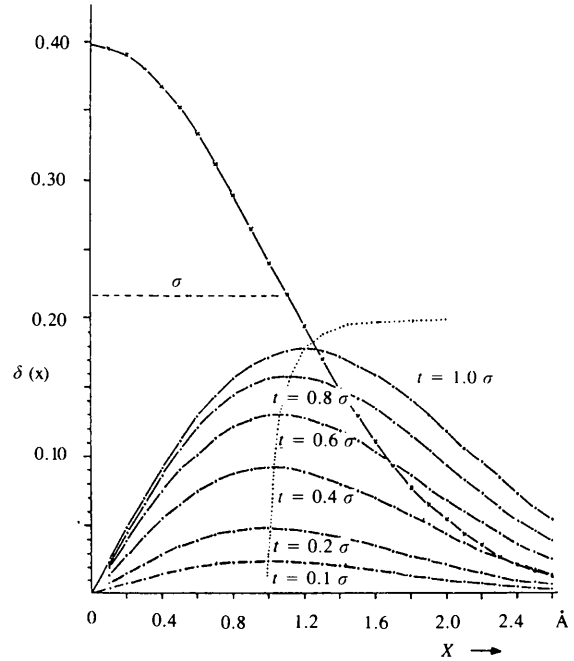

Fig. 3. Shape of the antisymmetric peaks in δ for different shifts t corresponding to the one-dimensional superstructure in Fig. 2 (only the positive part of the peak is represented). The stippled line through the maxima clearly shows that, for small shifts ($t \leq 1\sigma$), the maximum-to-minimum separation s is almost independent of t. To give an idea of the peak heights, the Gaussian 'atomic' peak is also reproduced.

The average and difference structures can be obtained from the partial Fourier syntheses

$$\bar{\rho}(\mathbf{x}) = V^{-1} \sum_{\mathbf{H}} \mathbf{F}_m(\mathbf{H}) \exp(-i2\pi\mathbf{H}\cdot\mathbf{x}) \qquad (3)$$

$$\delta(\mathbf{x}) = V^{-1} \sum_{\mathbf{h}} \mathbf{F}_s(\mathbf{h}) \exp(-i2\pi\mathbf{h}\cdot\mathbf{x}). \qquad (4)$$

In general, the phases $\varphi_m(\mathbf{H})$ necessary to calculate $\bar{\rho}$ can be easily derived by conventional direct methods using the intensities of the **H** reflections. According to (1), however, the determination of the superstructure also requires the solution of δ. Unfortunately, use of conventional direct methods to find the values of the phases $\varphi_s(\mathbf{h})$ directly from the intensities of the subset of superstructure reflections is rather difficult, since, unlike $\bar{\rho}$, the difference structure δ has positive and negative values. To overcome this difficulty, two different categories of method exist. Methods of the first category use the intensities of the main reflections to help to derive the phases of the superstructure reflections (Fan, He, Qian & Liu, 1978; Böhme, 1982; Fan, Yao, Main & Woolfson, 1983; Gramlich, 1984; Cascarano, Giacovazzo & Luić, 1988). Most direct-methods programs for solving superstructures belong to this category, *e.g. SAPI* (Fan *et al.*, 1990), *SIR* (Cascarano *et al.*, 1985) and *DIRDIF* (Beurskens *et al.*, 1990). In general, these programs solve a large variety of superstructures directly. Paradoxically, the advantage of exploiting the information provided by the main intensities can turn into a limitation for some specific applications, *e.g.* in the study of reconstructed surfaces where the main intensities are more difficult to analyze than the superstructure intensities due to the contribution from the bulk. The second category of methods does not suffer from this limitation because these methods only use the intensities of the superstructure reflections. Until now, there was only one method belonging to this category, *i.e.* the direct interpretation of the difference Patterson function (Takéuchi, 1972), which is briefly described in the next section. Recently, this method has experienced a revival in the determination of reconstructed surfaces (Rossmann *et al.*, 1992; Ferrer, Torrelles, Etgens, van der Vegt & Fajardo, 1995). Unfortunately, its interpretation is very often far from trivial. Consequently, efforts have been devoted to finding an alternative method suitable for being automated. This method is described in §2.

1.2. *The direct interpretation of the difference Patterson*

The difference Patterson function is defined as the integral (Takéuchi, 1972)

$$\delta P(\mathbf{u}) = V \int_V \delta(\mathbf{x})\delta(\mathbf{x}+\mathbf{u})\,\mathrm{d}\mathbf{x}. \qquad (5)$$

Unlike the normal Patterson function, $\delta P(\mathbf{u})$ contains positive and negative maxima, the form of which depends on the replacive or displacive nature of the superstructure (Figs. 1*d* and 2*d*). For *klassengleiche* superstructures, δP can be calculated with the synthesis

$$\delta P(\mathbf{u}) = \sum_{\mathbf{h}} |F_s(\mathbf{h})|^2 \exp(-i2\pi\mathbf{h}\cdot\mathbf{u}). \qquad (6)$$

The use of the difference Patterson function to solve order–disorder problems was introduced by Frueh (1953) and Buerger (1956). Later, more sophisticated approaches for interpreting the Patterson peaks were developed by Qurashi (1963) and Takéuchi (1972). Two notable applications are the solutions of the 13-fold hexagonal superstructure of $Cu_7As_6Se_{13}$ (Takéuchi & Horiuchi, 1972) and of bornite (Koto & Morimoto, 1975).

One advantage of this procedure is that the main reflections are not required in the calculation of δP, even though the knowledge of the average structure is of great help for its interpretation. The two principal disadvantages are, firstly, the cancellation of positive and negative peaks in δP, which can lead to incomplete vector sets, and, secondly, the difficulty of automating the whole interpretation procedure.

2. The interpretation of the difference Patterson δP by direct methods

Conventional direct methods rely on the similarity between ρ and ρ^2. This similarity is a consequence of the positivity and peaked nature of ρ. However, this is not true for δ. Since it contains positive and negative peaks, the power of conventional direct methods to solve it is weakened. One solution is to suppose that δ is similar to δ^3, *i.e.* if the structure factors of δ and δ^3 are, respectively, $\mathbf{E}_s(\mathbf{h}) = E_s(\mathbf{h})\exp[i\varphi_s(\mathbf{h})]$ and $\mathbf{C}(\mathbf{h}) = C(\mathbf{h})\exp[i\alpha(\mathbf{h})]$, the assumption is made that

$$\varphi_s(\mathbf{h}) \cong \alpha(\mathbf{h}). \qquad (7)$$

For convenience, let the set of superstructure reflections **h** (the E magnitudes of which have been normalized separately from those of the main or substructure reflections) be divided into two subsets, namely the subset containing the superstructure reflections with largest E magnitudes (**k** reflections) and the complementary one including the remaining superstructure reflections (**l** reflections). If Φ denotes the collectivity of phases of the **k** reflections, and if the resolution of the intensity data is high enough to produce well resolved peaks in δ, it follows that

$$\mathbf{C}_{\mathbf{h}}(\Phi) = \sum_{\mathbf{k}'}\sum_{\mathbf{k}''} \mathbf{E}_s(\mathbf{k}')\mathbf{E}_s(\mathbf{k}'')\mathbf{E}_s(\mathbf{h}-\mathbf{k}'-\mathbf{k}''). \qquad (8)$$

Hence, in view of (7), the amplitude $C_{\mathbf{h}}$ in terms of Φ may be approximated by

$$\begin{aligned} C_{\mathbf{h}}(\Phi) &= \mathbf{C}_{\mathbf{h}}(\Phi)\exp[i\alpha(-\mathbf{h})] \\ &\cong \exp[i\varphi_s(-\mathbf{h})] \\ &\quad \times \sum_{\mathbf{k}'}\sum_{\mathbf{k}''}\mathbf{E}_s(\mathbf{k}')\mathbf{E}_s(\mathbf{k}'')\mathbf{E}_s(\mathbf{h}-\mathbf{k}'-\mathbf{k}''). \end{aligned} \quad (9)$$

In parallel to Rius (1993), let $\delta P'$ and $\delta\mathcal{P}(\Phi)$ be the δP-type Fourier syntheses

$$\delta P'(\mathbf{u}) = V^{-1}\sum_{\mathbf{h}}[E_s(\mathbf{h}) - \langle E_s\rangle]\exp(-2\pi i\mathbf{h}\cdot\mathbf{u}), \quad (10)$$

$$\delta\mathcal{P}(\mathbf{u},\Phi) = V^{-1}\sum_{\mathbf{h}} C_{\mathbf{h}}(\Phi)\exp(-2\pi i\mathbf{h}\cdot\mathbf{u}), \quad (11)$$

the first one with the origin peak removed and the second one expressed in terms of Φ. Next, the integral measuring the coincidence between the observed $\delta P'$ and the calculated $\delta\mathcal{P}(\Phi)$ is defined:

$$\begin{aligned} Z_{\delta P'}(\Phi) &= V\int_V \delta P'(\mathbf{u})\delta\mathcal{P}(\mathbf{u},\Phi)\,\mathrm{d}\mathbf{u} \\ &= \sum_{\mathbf{h}}[E_s(\mathbf{h}) - \langle E_s\rangle]C_{\mathbf{h}}(\Phi), \end{aligned} \quad (12)$$

which can be also written as the sum of the products of the Fourier coefficients of $\delta P'$ and $\delta\mathcal{P}$. By introduction of the partition of $\mathbf{h}$ into $\mathbf{k}$ and $\mathbf{l}$, it follows that

$$\begin{aligned} Z_{\delta P'}(\Phi) &= \sum_{\mathbf{k}}[E_s(\mathbf{k}) - \langle E_s\rangle]C_{\mathbf{k}}(\Phi) \\ &\quad + \sum_{\mathbf{l}}[E_s(\mathbf{l}) - \langle E_s\rangle]C_{\mathbf{l}}(\Phi) \\ &= \sum_{\mathbf{k}}[E_s(\mathbf{k}) - \langle E_s\rangle]\exp[i\varphi_s(-\mathbf{k})] \\ &\quad \times \sum_{\mathbf{k}'}\sum_{\mathbf{k}''}\mathbf{E}_s(\mathbf{k}')\mathbf{E}_s(\mathbf{k}'')\mathbf{E}_s(\mathbf{k}-\mathbf{k}'-\mathbf{k}'') \\ &\quad + \sum_{\mathbf{l}}[E_s(\mathbf{l}) - \langle E_s\rangle]\exp[i\alpha(\mathbf{l})] \\ &\quad \times \sum_{\mathbf{k}}\sum_{\mathbf{k}''}\mathbf{E}_s(-\mathbf{k})\mathbf{E}_s(\mathbf{k}'')\mathbf{E}_s(\mathbf{k}-\mathbf{k}''-\mathbf{l}) \\ &= \sum_{\mathbf{k}}\mathbf{E}_s(-\mathbf{k})\Big\{\sum_{\mathbf{k}'}\sum_{\mathbf{k}''}X(\mathbf{k},\mathbf{k}',\mathbf{k}'')\mathbf{E}_s(\mathbf{k}')\mathbf{E}_s(\mathbf{k}'') \\ &\quad \times \mathbf{E}_s(\mathbf{k}-\mathbf{k}'-\mathbf{k}'') + \sum_{\mathbf{l}}[E_s(\mathbf{l}) - \langle E_s\rangle] \\ &\quad \times \exp[i\alpha(\mathbf{l})]\sum_{\mathbf{k}''}\mathbf{E}_s(\mathbf{k}'')\mathbf{E}_s(\mathbf{k}-\mathbf{k}''-\mathbf{l})\Big\} \end{aligned} \quad (13)$$

with

$$\begin{aligned} X(\mathbf{k},\mathbf{k}',\mathbf{k}'') &= 1 - (\langle E_s\rangle/4)[E_s(-\mathbf{k})^{-1} + E_s(\mathbf{k}')^{-1} \\ &\quad + E_s(\mathbf{k}'')^{-1} + E_s(\mathbf{k}-\mathbf{k}'-\mathbf{k}'')^{-1}]. \end{aligned} \quad (14)$$

$Z_{\delta P'}(\Phi)$ is expected to be a positive maximum for the correct Φ. By use of the same procedure as in Debaerdemaeker, Tate & Woolfson (1985), the new phase estimates maximizing $Z_{\delta P}(\Phi)$ can be found if the condition is solved for the limit of $Z_{\delta P'}(\Phi)$,

$$\partial Z_{\delta P'}(\Phi)/\partial\varphi_s(\mathbf{k}) = 0 \quad \text{for all } \mathbf{k}, \quad (15)$$

which, finally, leads to the $Z_{\delta P'}$ tangent formula

$$\begin{aligned} \varphi_s(\mathbf{k}) = \text{phase of } &\Big\{\sum_{\mathbf{k}'}\mathbf{E}_s(\mathbf{k}')\sum_{\mathbf{k}''}X(\mathbf{k},\mathbf{k}',\mathbf{k}'') \\ &\times \mathbf{E}_s(\mathbf{k}'')\mathbf{E}_s(\mathbf{k}-\mathbf{k}'-\mathbf{k}'') + \sum_{\mathbf{l}}[E_s(\mathbf{l}) - \langle E_s\rangle] \\ &\times \exp[i\alpha(\mathbf{l})]\sum_{\mathbf{k}''}\mathbf{E}_s(\mathbf{k}'')\mathbf{E}_s(\mathbf{k}-\mathbf{k}''-\mathbf{l})\Big\}, \end{aligned} \quad (16)$$

where the phases $\alpha(\mathbf{l})$ are periodically recalculated from $\mathbf{C}_{\mathbf{l}}(\Phi)$. The $Z_{\delta P'}$ tangent formula differs from the tangent formula given by Rius (1993) by the additional summation over $\mathbf{k}''$, *i.e.* it uses exclusively information provided by quartets and quintets. For the moment, the practical application of (16) is limited by the large number of four-phase relationships involved in its calculation, especially when the number of refined phases is large. In comparison with ρ, the difference structure δ contains less peaks. Consequently, the $Z_{\delta P'}$ tangent formula is expected to be effective in spite of its increased complexity.

Finally, it should be mentioned that refinement of phases maximizing $Z_{\delta P'}(\Phi)$ is not able to distinguish between $\delta(\mathbf{x})$ and its negative replica $-\delta(\mathbf{x})$. Effectively, if $\varphi_{\mathbf{h}} + \pi$ and $\alpha_{\mathbf{h}} + \pi$ are, respectively, the phases associated with the structure factors of $-\delta(\mathbf{x})$ and $-\delta(\mathbf{x})^3$, then it follows, after replacing them in (13), that $Z_{\delta P'}(\Phi) = Z_{\delta P'}(\Phi_n)$. Consequently, both solutions $\varphi_{\mathbf{h}}$ and $\varphi_{\mathbf{h}} + \pi$ are equally probable.

3. Test calculation

To demonstrate the capability of the $Z_{\delta P'}$ tangent formula to solve difference structures using only the intensities of the superstructure reflections, the double-layer mineral wermlandite was selected (Rius & Allmann, 1984). The crystal structure of wermlandite consists of two alternating layers: a brucite-like layer of composition $[\mathrm{Mg_7(Al_{0.57}Fe_{0.43})_2(OH)_{18}}]^{2+}$ and a completely ordered interlayer of composition $[\mathrm{(Ca_{0.6}Mg_{0.4})(SO_4)_2(H_2O)_{12}}]^{2-}$. The internal structure of the interlayer is shown in Fig. 4. The cell dimensions are $a = b = 9.303$, $c = 22.57$ Å and the space group is $P\bar{3}c1$ with $Z = 2$. Inspection of the diffraction pattern indicates that the layers with l even are much stronger (19% unobserved reflections) than the layers with l odd (47% unobserved reflections). The most relevant information extracted from the analysis of the intensity data is summarized in Table 1. The superstructure and the average structure have the same unit cell except for the length of the c parameter, which is doubled ($c = 2c'$). Since $n = 2$, both solutions δ and $-\delta$ will be equivalent. The c' distance corresponds to the separation between

Table 1. *Information about the average structure ($\overline{p}$) and the superstructure of wermlandite extracted from the intensity data*

The designation $k(2)$ (k = *klassengleich*) corresponds to that of Bärnighausen (1975) and indicates the type and index of symmetry reduction.

$P\bar{3}m1$ (cell of the $\overline{p}$ structure)
$h\ k\ l\ (l = 2n)$
510 reflections (98 unobserved)
$2c'$, $k(2)$ ↓
$P\bar{3}c1$ (superstructure cell)
$h\ k\ l$
779 reflections (224 unobserved)

brucite-like main layer and interlayer. According to their symmetry, the atoms in wermlandite can be grouped into the following:

(*a*) *Atoms with P$\bar{3}$m1 symmetry, i.e.* the main layer atoms and Ca^{2+}, S and the apical O atom of the SO_4^{2-} group. Since $P\bar{3}m1$ is the symmetry of $\overline{p}$, they will not contribute to δ and will not be further considered.

(*b*) *Atoms with P$\bar{3}$c1 symmetry, i.e.* the water molecules O(4) and O(5), and the atom O(6) forming the basis of the SO_4^{2-} group. Since the superstructure is of index $n = 2$, the corresponding averaged positions in $\overline{p}$ have half-weight (Fig. 2 in Rius & Allmann, 1984). These atoms appear as separate positive and negative peaks with half-weight in δ.

The solution of δ using only superstructure reflections has been done with a slightly modified version of *XLENS* (Rius, 1993) to allow the extra summaton over $\mathbf{k}''$. The 168 superstructure reflections with $d \geq 0.96$ Å were introduced in the program and the corresponding intensities normalized (overall B fixed at 3 Å^2). The program was selected to refine the phases of the 20 strongest E values (5060 quartets of the s–s–s–s type). The program automatically selected the 16 weakest reflections for their active use during the phase refinement (6368 quartets of the w–s–s–s type; $\langle E_s \rangle = 1.11$). The number of refined sets was 100 and the number of calculated cycles in each set was 13. The most probable solution was considered that with largest $Z_{\delta P'}(\Phi)$ and with $\sum_{\mathbf{l}} |\mathbf{C}_{\mathbf{l}}(\Phi)|$ as small as possible. The RESIDUAL figure of merit was not used owing to the difficulty of calculating the expected $C_{\mathbf{k}}$. This calculation requires the prior estimation of the probability distributions of the involved four-phase invariants (Hauptman, 1974), which is uncertain when at least one cross term is a main reflection. An extreme case is provided by the present example where all cross terms are main reflections. To compensate, a new figure of merit with no parallel in conventional direct methods is suggested based on the summation

$$\sum_{\mathbf{H}} |\mathbf{C}_{\mathbf{H}}(\Phi)|^2 = \sum_{\mathbf{H}} \left| \sum_{\mathbf{k}'} \sum_{\mathbf{k}''} \mathbf{E}_s(\mathbf{k}')\mathbf{E}_s(\mathbf{k}'')\mathbf{E}_s(\mathbf{H}-\mathbf{k}'-\mathbf{k}'') \right|^2, \tag{17}$$

which should be a small quantity for the correct solution.

Fig. 5 shows section ($x, y, z \cong 0.44$) of δ obtained from the solution selected according to the above criterion. Comparison of Figs. 4 and 5 shows the almost

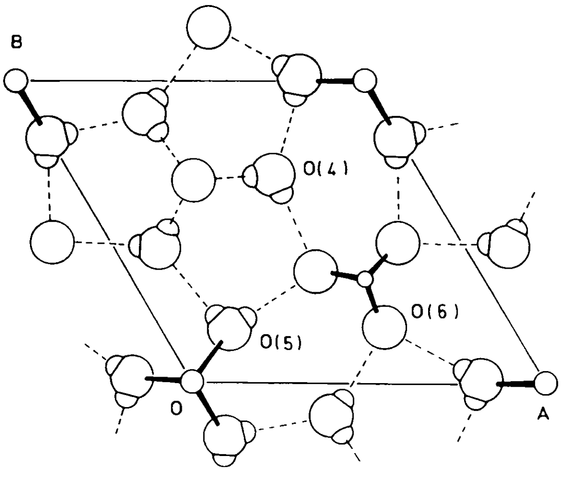

Fig. 4. Interlayer of wermlandite. For clarity, only the portion of the interlayer at $z \cong -0.08$ is represented. The rest is related by the inversion center at the origin. Ca^{2+} at (0, 0, 0) is octahedrally coordinated by $H_2O(5)$, which is H-bonded to O(6) (basis of the SO_4^{2-} group) and to $H_2O(4)$. Atom O(7) (apex of the SO_4^{2-} group) acts as acceptor of three H bonds from $H_2O(4)$ [S and O(7) at (2/3, 1/3, −0.057) and (1/3, 2/3, −0.005), respectively]. Only $H_2O(4)$, $H_2O(5)$ and O(6) have $P\bar{3}c1$ symmetry.

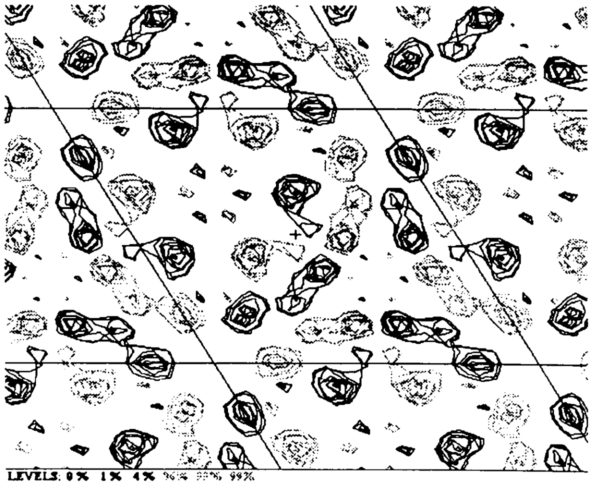

Fig. 5. Section ($x, y, z \cong -0.08$) of the difference structure δ of wermlandite obtained by applying direct methods to superstructure intensities only (black = positive, grey = negative values). The 20 phases of the strongest E values involved in the calculation of δ were refined with the $Z_{\delta P'}$ tangent formula. Notice the nearly exact correspondence between the positive peaks of δ and the positions of $H_2O(4)$, $H_2O(5)$ and O(6) in Fig. 4. Image obtained with *FAN* (Vernoslova & Lunin, 1993).

exact correspondence of the positive peaks of δ with the positions of $H_2O(4)$, $H_2O(5)$ and O(6). Only O(6) shows a split peak, the stronger one corresponding to the correct position of O(6). This result clearly demonstrates the possibility of solving the difference structure of wermlandite by refining the phases of the superstructure reflections with the $Z_{\delta P'}$ tangent formula.

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