Acta Cryst. (1997). A**53**, 475–483

A Method for Obtaining a Possibly Unique (Unambiguous) Crystal Structure Solution using Multiple Resonant Scattering Data

KARL F. FISCHER* AND KATRIN PILZ

Institute of Crystallography, University of Saarbrücken, D 66041 Saarbrücken, Germany

(Received 26 July 1996; accepted 3 March 1997)

Abstract

A sequence of steps for determining a crystal structure, possibly without ambiguities, is presented. The prerequisites are: centrosymmetry (at present) and two different anomalous scatterers, a_1, a_2. Their partial structure amplitudes $|F_{a1}(hkl)|$ and $|F_{a2}(hkl)|$ are separated by multiple-wavelength measurements (MAD). The core part of the method is a recursive algebraic technique applied to the geometrical part of these structure amplitudes from central reciprocal-lattice rows. At least $m + 1$ reflections are necessary at each row if $2m$ atoms of *e.g.* a_1 are in a unit cell with space group $P\bar{1}$. For each partial structure of a_1 and a_2 atoms, respectively, the algebra finds all homometric and pseudohomometric solutions and presents the corresponding signs for each $F_a(hkl)$ used. Regions of confidence for atomic coordinates are given. Five reciprocal-lattice rows (or more) suffice for a 'tomographic' location of all atoms a_1 and a_2 in three dimensions. The two independently determined partial structures for a_1 and a_2 are then aligned to the same origin and moduli plus signs of the remaining partial structure factors of the non-resonant atoms are determined. Various aspects of the method are discussed by application to the Cu_3SbSe_3 structure, an example exhibiting partial pseudosymmetry.

1. List of symbols and definitions

h, i, j, k, l	Running indices
m	No. of (symmetrically) independent atoms in the unit cell, also of a partial structure
a, a_1, a_2	Atoms that may act as anomalous scatterers
λ_a	λ of absorption edge for a atoms
$f(\lambda, \sin\theta/\lambda)$	Atomic scattering factor $= f^0(\sin\theta/\lambda) + f'(\lambda) + if''(\lambda)$
B	Displacement factor coefficient
F	Structure factor
F_a	Partial structure factor of a atoms. Its modulus $\lvert F_a\rvert$ is obtained by measuring $\lvert F\rvert^2$ at various wavelengths close to an absorption edge λ_a of a (plus perhaps at a rather short wavelength and plus at least one Bijvoet mate for non-centrosymmetric structures) according to Karle (1980)
F_{a1}, F_{a2}	Partial structure factors for atoms a_1, a_2 based on f_{a1}, f_{a2}
F^0_{a1}, F^0_{a2}	As above, based on f^0_{a1}, f^0_{a2}
$\lvert F_1\rvert$	Structure amplitude used for obtaining $\lvert F_{a1}\rvert$ in separation procedure (Karle, 1980) no. 1 in a structure with anomalous scatterers a_1, a_2 according to $F_1 = F_{a1} + F_{1n}$ with $F_{1n} = F^0_{a2} + F_{1n}$
s	Sign of structure factor or partial structure factor or of its geometrical part
s_r	Relative sign of two partial structure factors according to $F = F_a + F_n = s_a\lvert F_a\rvert + s_r s_a\lvert F_n\rvert$ with $\lvert F\rvert = \lvert F_a\rvert + s_r\lvert F_n\rvert$
$F_{1n} = F_{2n} = F_{nn}$	Structure factor of atoms always non-resonating, *i.e.* of atoms neither a_1 nor a_2
F_n	Structure factor of normal scatterers for a structure with only one kind of a atom (at the wavelength used for measurement)
g	Geometrical part (modulus only) of the structure factor for a monoatomic partial structure of the asymmetric unit having m atoms. In space group $P\bar{1}$: $g_{\mathbf{h}} = g(hkl) = \left\lvert\sum_{j=1}^{m}\cos(2\pi\mathbf{h}\cdot\mathbf{r}_j)\right\rvert$ $(\mathbf{h} = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^*,$ $\mathbf{r} = x\mathbf{a} + y\mathbf{b} + z\mathbf{c})$ For a central reciprocal-lattice row, *e.g.* $h00$ reflections: $g_h = g(h00) = \left\lvert\sum_{j=1}^{m}\cos(2\pi hx_j)\right\rvert$
g_a	g for a atoms
P_h	Power sum of the $\cos(2\pi x_j)$ with power h
$R(c)$	Polynomial in $c = \cos(2\pi x)$
Q_i	Coefficients of $R(c)$

Acta Crystallographica Section A
ISSN 0108-7673 © 1997

$\Sigma = \sum_h w_h \Delta_h^2$	$\Delta_h = S\lvert F_{h,\mathrm{obs}}\rvert - \lvert F_{h,\mathrm{cal}}\rvert$ (or $\lvert F_h\rvert^2$ if preferred), w_h = weight of observed $\lvert F_h\rvert$ and h here representing h, k, l
S	Scaling factor for experimental F or F_a
σ	(Standard) error

2. Introduction

Two essentially different cases exist for non-unique crystal-structure determinations: homometry and pseudohomometry (provided we do not deal with the question of polarity or enantiomers, which can both be solved by standard methods, *e.g.* using f'' of anomalous scatterers). True homometric cases are rather rare and exist due to special symmetry conditions of the space group. Hence, they can be theoretically investigated and thus be predicted in principle – however not always easily: Two (or more) different arrangements of the same atoms have the same interatomic vector set. Therefore, the different structures produce identical scattering intensities and cannot be discriminated without knowing phases of some relevant *F*(*hkl*). In principle, the simple case of homometric pairs can be solved by just one phase (in analogy to the sign of a single Bijvoet difference being decisive for enantiomer discrimination). Homometry is a 'classical' problem and was first treated by Patterson (1939).

With the term 'pseudohomometry' we want to describe a situation that occasionally exists (unfortunately, however, more often than hoped for or expected by crystallographers): *i.e.* a structure solution may converge, *e.g.* by a least-squares fit, into a 'false' minimum that is neither the only one nor represents the lowest $\Sigma = \sum_h w_h \Delta_h^2$ in the hyperplane on the multidimensional parameter space. Two situations may occur: If Σ (or any type of corresponding *R* factor) is higher than expected from the average of experimental $\sigma(|F_h|)$, the researcher may become suspicious and look for a 'better' solution, which then may converge into the 'true' minimum of Σ. If, however, Σ is not substantially larger than expected – and correct assessment of experimental errors of intensities is sometimes hard to obtain – the minimum may not be recognized as a false one. In this situation (without smaller σ's and/or higher reflection orders available), the experimentalist usually contents himself with his structure model until somebody else using another data set finds a better (and hopefully true) minimum.

3. Initial considerations

For the following, we shall restrict ourselves to the pure geometry of a crystal-structure model and will not consider atomic displacements. Two general ways for evaluating all possible geometrical solutions appear obvious: In direct space, one could vary the fractional coordinates *x*, *y* and *z* of all independent atoms $j = 1, \ldots, m$ in appropriate steps from 0 to 1 (one coordinate between 0 and 1/2 for space group $P\bar{1}$) and calculate Σ for each combination, thus mapping Σ as a function of all possible atomic vectors $\mathbf{r}_j$ in the half unit cell. The other way would be varying in reciprocal space all reflection phases (for a $\bar{1}$ structure: trying all sign variations in the asymmetric part of reciprocal space) for computing electron-density maps (or *E* maps for restricted data sets). It is evident that both ways are not feasible with present day computers, and if they were (*e.g.* for an *hkl* set limited to perhaps a few hundred data), they would be ways of 'brute force'. Let us therefore begin first with tailoring the problem into a manageable size, *i.e.* we shall restrict the discussion to:

(i) centrosymmetric structures: $|F|$ signs instead of phases, and only space group $P\bar{1}$ in order to avoid complications due to other symmetry elements: this does not affect the principle and any other centric space group can be handled individually;

(ii) partial structures of one atomic species only: their partial $|F|$ can be reduced to represent (relatively) few identical point scatterers without the necessity to approximate an averaged atomic scattering power;

(iii) treating only one dimension in a single step: then, *m* independent atoms cell^{-1} require only *m* unknown (scalar) coordinates to be determined (instead of vectors with three components).

Secondly, we will address some prerequisites and desires:

(i) Partial structure factors of an atomic species *a* can be obtained for anomalous scatterers: from three or more measurements at different λ's (*e.g.* at $\lambda > \lambda_a$ and one close to an absorption edge λ_a), the procedure of Karle (1980) permits each $|F|$ to be separated into $|F_a|$, $|F_n|$, and the relative sign s_r between F_a, F_n (F_n representing the non-resonant atoms, $F = F_a + F_n$ or $|F| = |F_a| + s_r|F_n|$, respectively). The MAD technique (Hendrickson, 1985) works also on non-centrosymmetric structures. For powder measurements, Prandl (1990, 1994) developed techniques for separating and evaluating $|F_a|$. For details on single crystals, see also Pilz (1995).

(ii) A tool is needed for deriving *e.g.* the *x* coordinates of species *a* from the $|F_a(h00)|$ and finding all possible solutions, be they homometric or pseudohomometric. To this purpose, we shall briefly describe a 'recursive algebraic technique'.

(iii) If possible, a measure of confidence or 'figure of merit' should be assigned to each possible solution.

(iv) Individual standard deviations are wanted for all atomic coordinates.

(v) In a later stage, treated in the 'point-tomography' section, the *x* coordinates have to be combined with *y* and *z* parameters determined independently from 0*k*0 and 00*l* data.

(vi) The three-dimensional partial structures must be referred to the same cell origin.

4. Recursive algebraic technique

An algorithm was developed for solving one-dimensional centrosymmetric crystal structures or projections for (at present) a single atomic species *a* (Knof, 1989; Pilz *et al.*, 1994; Fischer & Pilz, 1995; Pilz & Fischer, 1996). It is based on a series of 'harmonic' partial structure amplitudes $|F_a(h00)|$ obtained from the separating process mentioned above. h is assumed to vary in unit steps from 1 to $m+1$ if m independent a atoms are to be located. [For simplicity of this brief description, no special positions are considered – a more detailed and thorough paper by Pilz & Fischer, presenting also proofs of the short mathematics below has been submitted (Pilz & Fischer, 1997).] The $|F_a|$ are expected to be approximately on an absolute scale, and the (overall) Debye temperature factor $T_h = \exp(-B|\mathbf{h}|^2/4)$ is assumed to be known.

The geometrical term $s_{a,h}g_{a,h}$ of $F_a(h00)$ represents the 'point' structure of the m independent a atoms. For the $h00$ reflections, its modulus

$$|g_{a,h}| = \left|\sum_{j=1}^{m}\cos(2\pi h x_j)\right|$$

is obtained from the $|F_a(h00)|$ or from the $|F_a^0(h00)|$, respectively, by

$$g_{a,h} = |F_a^0(h00)|/2f_a^0(\sin\theta_h/\lambda)T_h.$$

It can then be shown that a polynomial $R(c) = R[\cos(2\pi x)]$ exists with m roots representing all $\cos(2\pi x_j)$. Owing to centrosymmetry, the x_j are obtained unambiguously. [It follows that $R(c)$ can be simply transformed into a corresponding $R(x)$ providing directly all coordinates of the a atoms, see Fig. 1.] $R(c)$ is computed from $m+1$ s_hg_h values in a double recursive procedure: First, they are converted into

$$P_h = \left[s_hg_h - \sum_{l=1}^{[h/2]}(-1)^l 2^{h-1-2l}\frac{h}{h-l}\binom{h-l}{l}P_{h-2l}\right] \times 2^{1-h}$$

with $[h/2]$ denoting the integer part of $h/2$. Q_i according to

$$Q_i = \left[\sum_{l=0}^{i-1}(-1)^{i-l-1}P_{(i-l)}Q_l\right]\Big/ i$$

are coefficients of $R(c)$:

$$R[\cos(2\pi x)] := \sum_{i=0}^{m}(-1)^i Q_i \cos^{m-i}(2\pi x).$$

The signs s_h of all g_h, necessary for calculating P_h with $h > 1$, are obtained by checking all 2^m variations of s_h, $h = 2,\ldots,m+1$ by means of a determinant D_1 that vanishes for the correct sign variation in the case of theoretically exact g_h:

$$D_{1c} = 0.$$

D_1 is defined by

$$D_1 = \begin{vmatrix} P_1 & 1 & 0 & \cdots & 0 & 0 \\ P_2 & P_1 & 2 & \cdots & 0 & 0 \\ \vdots & \vdots & \vdots & \ddots & \vdots & \vdots \\ P_m & P_{m-1} & P_{m-2} & \cdots & P_1 & m \\ P_{m+1} & P_m & P_{m-1} & \cdots & P_2 & P_1 \end{vmatrix}.$$

For g's with increasing experimental errors, D_{1c} remains 'small', but the relative contrast against all other possible D_1's lessens. If two (or perhaps more) "small D_{1c}'s" appear with equal or almost equal values (or zeros, respectively), the two (or perhaps more) corresponding sign variations indicate possible homometries or pseudohomometries. For D's of higher rank, see Pilz & Fischer (1997). In many cases, a pseudohomometric solution can be excluded by introducing into the sign determination one or more higher harmonics g_h with $h > m+1$, which eliminates the sign ambiguity for one of the lower harmonics (as is to be expected from standard structure solution practice employing high-order data). Therefore, this algebra is well suited for solving even some pseudosymmetric structures. As one may judge from the polynomials R obtained with assumed random errors introduced into the g_h data, the method also seems to be fairly robust against considerable experimental errors, which are inevitably caused by the separation procedure of $|F|$ into $|F_a|$, $|F_n|$ and s_r (see *e.g.* Fig. 1).

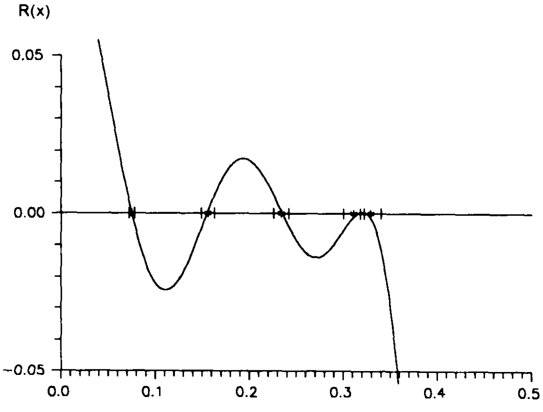


Fig. 1. Polynomial R plotted *versus* x for a one-dimensional structure with coordinates $x_1 = 0.075$, $x_2 = 0.155$, $x_3 = 0.235$, $x_4 = 0.315$, $x_5 = 0.325$ [error bars show standard errors of coordinates caused by assumed errors $\sigma(g_h) = 0.1g_h$].

To sum up: the one-dimensional recursive algebraic technique is based on a series of structure amplitudes $2g_h$ from $2m$ identical points (with unit weight), projected parallel to **b** and **c** onto the x axis. The g's are transformed into a function $R(x)$ representing the x_j locations as roots. The correct sign variation is found by varying s_h for all $h > 1$ and using determinants D as criterion for the correct result. Individual (standard) errors for the coordinates, found by Monte Carlo computations, are small. Having processed also the $|F_a(0k0)|$ and $|F_a(00l)|$, all x, y and z coordinates of the a-atom partial structure are known, not, however, in which combination they are arranged.

5. Three-dimensional point tomography of the partial structure

Attaching each y_i coordinate ($i = 1,\ldots,m$) to one x_j or $-x_j$ ($j = 1,\ldots,m$) is performed *via* a rather naive approach that works only if sufficient spatial resolution is obtained in the one-dimensional projections: We employ a 'diagonal' in the reciprocal ($hk0$) plane, *e.g.* the $hh0$ reflections. Their $|F_a|$ are treated with the same algebra. The only difference is in the determination of all $m + 1$ signs, because the origin has been fixed already. (If, in some cases, no unique x_j, y_i combination can be obtained, another diagonal, say $h,2h,0$ or $2h,h,0$ can be used, additionally to or instead of $hh0$.) In complete analogy, a diagonal with an l component (*e.g.* $h0h$ or $0kk$) serves for assigning correct z_k or $-z_k$ ($k = 1,\ldots,m$) to the pairs of x, y coordinates established before. The three-dimensional partial structure of an anomalous scatterer (or any single atomic species separated otherwise) can thus be determined using (at least) five central reciprocal-lattice rows, each with $m + 1$ 'harmonic' reflections (starting with the first order). Since only 2^m variations of signs per row (or 2^{m+1} for the two diagonals) are necessary, their number is by far less than that in the 'brute-force' technique mentioned above.

We like to use the term 'point tomography' for combining the x_j with the y_i and finally the z_k ($j, i, k = 1,\ldots,2m$) because our approach is a reduced analogue to the tomographic method widely applied in medicine, material science and other non-destructive investigations: a three-dimensional density function is determined or approximated (representing *e.g.* X-ray absorption) by numerically evaluating one- or two-dimensional projections. In our case, we deal only with an arrangement of m (or $2m$) identical points in half (or full) cell volume. Provided no ambiguity is caused by two (or more) points accidentally coinciding in one of the three main projections or in particular in one of the diagonals, two of the latter suffice for correct assignment of each j to one of the i's and k's. [In some space groups and also due to special positions occupied, the selection of diagonals has to be carefully considered because a diagonal working well in $P\bar{1}$ is not necessarily suitable for all space groups. See the 'example' below, where a space diagonal (hhh reflections) was used.]

By a combination of the algebraic and the tomography techniques, all possible solutions are detected. Also, errors of individual atomic coordinates may be assessed by Monte Carlo computations [details are found in Pilz & Fischer (1997)]. Of course, each of the solutions found can also be refined, for example, on the basis of $|F_a(\mathbf{h})|$ by least squares. This may not only result in improved coordinates, scale and displacement factors but may also exclude one or more 'false' solutions. It is particularly suited if more (higher) harmonic reflections are available than required by the algebra. The partial structure may thus be considered either as uniquely defined (within estimated individual coordinate uncertainties) or all possible pseudohomometric solutions (based on the rather limited experimental data) are found, also with error regions. (In this case, employing additional data can only decrease both number of solutions and error limits.)

6. Two anomalous scatterers, origin adjustment of partial structures

Consider a centrosymmetric structure containing two different kinds of atoms a_1 and a_2 whose absorption edges are accessible plus an arbitrary number of normal scatterers n. Let us consider all structure factors F to be reduced to $f' = f'' = 0$ for both a atoms:

$$F^0 = F^0_{a1} + F^0_{a2} + F_{nn}.$$

$|F^0_{a1}|$ and $|F^0_{a2}|$ are assumed to be separated by selecting appropriate X-ray energies for the measurements. The two partial structures of a_1 and a_2 are obtained independently by the method described above.

In space group $P\bar{1}$, adjusting both partial structures to the same cell origin means selecting 1 of 8 possibilities: For *e.g.* the $h00$ reflections, the origin for the x parameters of the a_1 and a_2 atoms may or may not differ by 1/2. As a result of the algebraic technique, the signs s_{a1} of all $|F^0_{a1}(h00)|$ are known and, by virtue of the relative signs s_{r1} (obtained from the first separation procedure after Karle), also the signs of the corresponding $|F^0_{1n}| = |F^0_{a2} + F_{1n}|$ and of $|F^0_1|$:

$$s_{a1}|F^0_{a1}| + s_{a1}s_{r1}|F^0_{a2} + F_{1n}| = F^0_1.$$

This permits F_{1n} to be obtained from the first separation as

$$F_{1n} = F^0_1 - F^0_{a1} - s_{a2}|F^0_{a2}|$$

by introducing the modulus and sign of F^0_{a2} obtained from the tomography of the a_2 atoms. In direct analogy, from the second separation of $|F^0_2|$, $|F^0_{a2}|$ and $s_{r2}|F^0_{a1} + F_{2n}|$ are known, leading to

$$s_{a2}|F^0_{a2}| + s_{a2}s_{r2}|F^0_{a1} + F_{2n}| = F^0_2$$

and thus to

$$F_{2n} = F_2^0 - F_{a2}^0 - s_{a1}|F_{a1}^0|.$$

Both independently obtained F_{1n} and F_{2n} must be identical for h even within experimental errors. For odd orders, $F_{1n} = F_{2n}$ only if both partial structures refer to the same origin in x, which may be adjusted by adding 1/2. As a by-product, amplitudes and signs $F_{1n} = F_{2n} = F_{nn}$ are known for $h00$ reflections. The same process, applied to the $0k0$ and $00l$ data, adjusts the origin of the a_2 structure to that of a_1 in all three dimensions. Finally, a set of s_{a2} (or s_{a1}) of the 'diagonal' data is corrected if necessary.

7. Jagodzinski's idea on unique structure determination and its Patterson aspect

Jagodzinski (1971) published a theoretical paper demonstrating that, for any crystal structure with two (chemically different) anomalous scatterers a_1 and a_2, a unique structure solution can be obtained by means of diffraction intensities taken at six wavelengths. The wavelengths (three around the absorption edge of each a atom) should be selected such that sufficient intensity contrast due to f' and f'' is obtained. All measurements must be properly scaled. Knof (1989) reformulated this idea by casting it into a system of linear equations. Since, however, at present only a small amount of knowledge exists on how well they are conditioned for practical solution, in particular in the presence of experimental errors, this approach did not foster much further development. Prandl (1990) devised a principle for solving non-centrosymmetric structures based on two anomalous scatterers.

Let us consider a centrosymmetric structure having a_1, a_2 plus n atoms analogous to the last section. We assume the partial structures of both anomalous scatterers to be solved and origin aligned as before. Then, owing to the last paragraph in the tomography section, the two partial structures a_1 and a_2 have been tested for pseudohomometry. Provided no such problem is found for the n atoms as well, the structure model obtained can be considered unique within the limits of error obtained for each partial structure. Following the result of the last section, partial structure factors F_n are then known by modulus and sign after the origin alignment. This applies directly to any hkl whose $|F|$ has been subjected to the separation of $|F_{a1}|$ and $|F_{a2}|$. In principle, all measured $|F(hkl)|$ can be separated into F_{a1}, F_{a2} (computed from *e.g.* refined respective partial structures) rendering F_{nn}. Therefore, the n-atom arrangement can also be assumed to be determined without ambiguity, save the errors propagated into the $F_{nn}(hkl)$ by the separation calculations.

From a Patterson point of view, Jagodzinski's idea can be described best by using the vector set matrix (Buerger, 1959) with elements $w_{ij}\mathbf{u}_{ij}$, each representing a vector $\mathbf{u}_{ij}$ between two atoms at locations $\mathbf{r}_i$ and $\mathbf{r}_j$ and weights proportional to the products of their respective (forward-) scattering factors. The matrix (Fig. 2) is divided into sections by separating the $2m_1$ atoms of type a_1 from the $2m_2$ atoms of type a_2 and the $2m_n$ atoms of normal scatterers n. For $P\bar{1}$, each half Patterson $P(\mathbf{u})$ consists of six sections (apart from the trivial peak at $\mathbf{u} = \mathbf{0}$), four of which can be calculated after solution of a_1 and a_2 partial structures: vector sets $a_1 \Leftrightarrow a_1'$, $a_2 \Leftrightarrow a_2'$ and $a_1 \Leftrightarrow a_2$, plus vectors $n \Leftrightarrow n'$ from (doubly determined) $|F_{nn}|^2$. Subtracting these components from $P(\mathbf{u})$ leaves

$$\begin{aligned} P(\mathbf{u}) - P(a_1, a_1') - P(a_2, a_2') - P'(a_1, a_2) - P(n, n') \\ = P'(a_1, n) + P'(a_2, n), \end{aligned}$$

denoting by P' corresponding vector sets that are not partial Patterson functions in the true sense. The right side of this equation (positive definite in the whole cell volume) can be deconvoluted using as search model all $\mathbf{r}_{a1}$ and $\mathbf{r}_{a2}$ positions [properly weighted in analogy with Fischer (1981, 1987)]. The result is the $\mathbf{r}_n$ set. If all $\mathbf{r}_n$ are uniquely obtained, the whole structure has been determined without ambiguity. (The solution of the n-atom structure can, of course, be achieved by any suitable method.)

In principle, one of the six λ's mentioned by Jagodzinski can be omitted if a rather short wavelength λ_0 is used, for which none of the atoms exhibits significant f' and f''. In a centrosymmetric case, contrast merely due to f' of a_1 and a_2 is sufficient. (For non-centrosymmetric structures, the contribution of f'' to the Bijvoet differences is also required.) In planning an actual experiment, the wavelength selection deserves consideration with respect to possible cross-over influence on $|F|^2$ of, say, changes in f'_{a1} associated with non-zero differences of f'_{a2} or f''_{a2}.

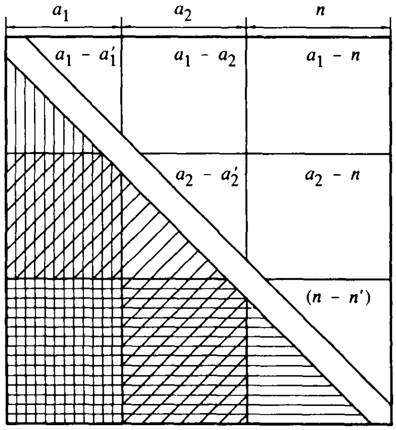


Fig. 2. Patterson matrix for a structure with two different anomalous scatterers a_1, a_2 and normal scatterers n.

Table 1. *Atomic positions of* Cu_3SbSe_3

First line of each atomic site: Parameters from Pfitzner (1995) with estimated standard uncertainties in parentheses.
Second line: Coordinates obtained by the recursive algebraic method with theoretical partial g (no errors assumed). Numbers of reflections used for determining signs and parameters respectively in parentheses (s/x).
Third line: As above, with errors assumed to be: g_1 3%, g_2 5%, g_3 7%, g_4 10% for Se and Sb atoms and 6, 8, 10, 12% for Cu. In parentheses: coordinate errors estimated from Monte Carlo computations.
Fourth line: As above with experimental data from Table 2 (B values assumed as listed).
Fifth line: Coordinates after anisotropic joint refinement of 52 parameters against all eight (full) data sets measured at eight wavelengths (total of 1540 reflections).

	x	y	z	B (Å^2)
Cu(1)	0.0913 (2)	0.0427 (2)	0.2446 (4)	3.0
	0.0913 (4/3)	0.0427 (4/3)	0.2446 (4/3)	
	0.090 (2)	0.038 (9)	0.234 (20)	
	0.092	–*	0.25	3.0
	0.0905 (2)	0.0424 (1)	0.2435 (2)	2.52
Cu(2)	0.1912 (4)	1/4	0.4309 (4)	3.0
	0.1912 (4/3)	1/4	0.4309 (4/3)	
	0.186 (5)	1/4	0.431 (5)	
	0.212	–*	0.415	3.0
	0.1905 (2)	1/4	0.4305 (2)	2.76
Sb	0.2511 (2)	1/4	0.8885 (2)	1.61
	0.2511 (2/1)	1/4	0.8885 (2/1)	
	0.245 (8)	1/4	0.888 (7)	
	0.242 (12)	1/4	0.905 (17)	1.5
	0.2516 (1)	1/4	0.8886 (1)	1.00
Se (1)	0.0060 (2)	1/4	0.1357 (3)	1.66
	0.0060 (4/3)	1/4	0.1357 (4/3)	
	0.002 (4)	1/4	0.137 (8)	
	0.003 (8)	1/4	0.128 (16)	1.5
	0.0063 (2)	1/4	0.1360 (2)	1.10
Se (2)	0.1611 (2)	0.0658 (1)	0.6553 (2)	1.5
	0.1611 (4/3)	0.0658 (4/3)	0.6553 (4/3)	
	0.162 (5)	0.066 (5)	0.655 (17)	
	0.155 (10)	0.052 (19)	0.662 (24)	1.5
	0.1615 (1)	0.0661 (1)	0.6553 (1)	0.95

* Not determined.

Table 2. *X-ray energies and lattice rows used for determining the partial structures of Se and Sb atoms*

Se			Sb		
E (keV)	f'		E (keV)	f'	
12.55	−4.347		29.20	−2.892	
12.58	−4.677		30.25	−4.372	
12.60	−4.982		30.45	−6.014	
12.62	−5.420				
12.64	−6.207				
Main rows (class 1)					
$2h,0,0$	$0,2k,0$	$0,0,2l$	$2h,0,0$	$0,2k,0$	$0,0,2l$
1,. . .,5	1,. . .,3	1,. . .,5	1,. . .,4	1,. . .,4	1,. . .,4
Diagonals (class 2)					
$h0h$	$0kk$	hhh	$h,0,2h$	$0kk$	hhh
1,. . .,5	1,. . .,5	1,. . .,3	1,. . .,3	1,. . .,4	1,. . .,3

8. Example and discussion

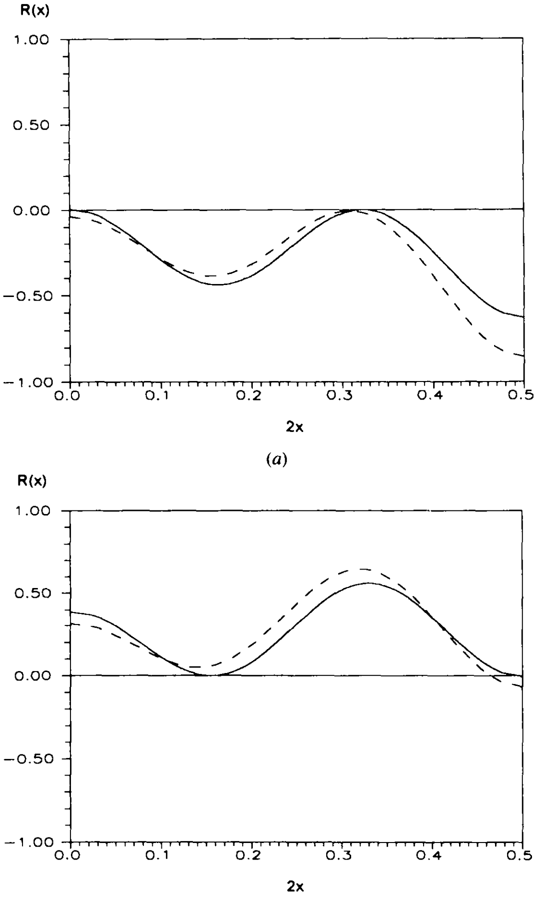
We used the compound Cu_3SbSe_3 as a test object for the method outlined above. Its crystal structure has been determined recently by Pfitzner (1995) (*Pnma*, $Z = 4$, $a = 7.9984$, $b = 10.6232$, $c = 6.8416$ Å, Table 1). It exhibits elements of pseudosymmetry and (one-dimensional) pseudohomometry.

We separated the Se (as a_1 atoms) and Sb (as a_2) by measuring with X-ray energies close to the respective K edges (Table 2). A multiple-wavelength 'joint' refinement (Spilker, 1983) of 52 parameters (12 coordinates, 24 anisotropic vibration parameters, 8 scale and isotropic extinction coefficients for the 8 data subsets) against 1540 independent $|F_{\rm obs}|^2$ resulted in $R = 0.042$, $R_w = 0.078$ and a goodness of fit GOF = 2.92. (For 8 refinements at individual wavelengths with 38 parameters *versus* 181–192 reflections, we obtained $R = 0.027$–0.033, $R_w = 0.041$–0.051, GOF = 1.07–1.70.) We used the scale factors from the refinement [which is a 'weak point' and deserves attention as treated in Pilz & Fischer (1997)]. We estimated B (overall) to be 1.5 Å^2.

From theoretical $g(hkl)$ without errors, computed from parameters of the structure determination by Pfitzner (1995), we determined the two partial structures for Se and Sb (line 2 in Table 1) with the method described above, and also from $g(hkl)$ with assumed errors (line 3). The differences between our experimental g's and the theoretical ones turned out to be larger than those used in the Se test computations: For 26 $g_{\rm Se,obs}$ (22 $g_{\rm Sb,obs}$) from 6 central reciprocal-lattice rows each, compared with the respective 'theoretical' g's, we obtained R factors of 0.37 (0.38). We solved the Sb partial structure with the algebraic method and succeeded in obtaining the Se coordinates from six reciprocal-lattice rows (see Table 2) by employing 26 g's and omitting some measured harmonics higher than those listed in Table 2. Therefore, the results obtained for the Se and Sb positions from their respective $g_{\rm obs}$ (line 4 in Table 1) exhibit considerably larger Monte Carlo error regions (compared with line 3). Nevertheless, both partial structures appear rather well defined considering the restricted number of data used (see Table 2) and comparing it with an (unrefined) trial structure model to be obtained from a Patterson or E map. From the amount of experimental errors in the $g_{\rm obs}$ produced by the separation procedure, the algebraic method appears to be fairly robust although it deserves careful and critical handling.

For two reciprocal-lattice rows, $g_{\rm Se}(2h,0,0)$ and $g_{\rm Sb}(0kk)$, unambiguous results were obtained only after origin alignment between both partial structures. Fig. 3 shows the corresponding polynomials for the correct solution (a) after origin alignment, and the biased alternative (b), from both theoretical and experimental $g_{\rm Se}(2h,0,0)$. Numerous similar one-dimensional pseudohomometries as well as elements of pseudosymmetry were detected. [For instance, the difference in z of Se(1) and Se(2) being close to 1/2 causes Se–Se non-Harker vectors to show up in a Harker plane for all atoms. This explains perhaps the high standard errors of the z values in line 4 (Table 1).] All pseudohomometries could be resolved without doubt, except one coordinate shift of Sb along x, which came out smaller than 1/4 (instead of larger), however still within its standard deviation from the value of line 5 (Table 1), whose numbers we considered as being 'true' compared with those found by the algebra. The signs of some partial structure factors for the Cu atoms were also found. A closer look at the parameters of line 4 reveals:

(i) None of them differs (denoted by Δ) from the corresponding 'true' one by more than one standard deviation. Averaged over the seven independent Sb, Se parameters, Δ/σ equals 0.54 (with a maximum of 0.965). The Monte Carlo calculation of σ apparently produces valid results.



(*a*)

(*b*)

Fig. 3. (*a*) $R(2x)$ for the correct sign variation [$s(200) = +1$, $s(400) = -1$, $s(600) = +1$, $s(800) = +1$] of the $g_{\rm Se}(h00)$ (solid curve: theoretical; dashed curve: experimental). (*b*) $R(2x)$ for the biased alternative sign variation [$s(200) = +1$, $s(400) = +1$, $s(600) = -1$, $s(800) = -1$] of the $g_{\rm Se}(h00)$ (solid curve: theoretical; dashed curve: experimental).

(ii) The average of Δ, multiplied by the respective lattice constants, is 0.07_4 Å (maximum 0.15 Å).

(iii) The three-dimensional deviation from the 'true' position is found to be 0.13 Å for Sb, and 0.06 and 0.16_5 Å for Se, respectively.

We consider this result as rather promising, although the example is a very small structure. More details on the structure of Cu_3SbSe_3 and its determination will be published in a forthcoming joint paper with Pfitzner.

9. Conclusions

For the method described above, we shall briefly summarize first its physical and mathematical basis. We assume that, for each central reciprocal-lattice line selected, the partial structure amplitudes $|F_a(h)|$ for $h = 1, \ldots, m + 1$ can be obtained and reduced to their respective geometrical part g_h. For centrosymmetric structures, the corresponding measurements are done at $\lambda > \lambda_a$.

In practice, the inherent problems are:

(i) Scale S and (overall) displacement factor B must be known, at least approximately. This can be achieved by applying Wilson's statistics to an approximately complete reflection data set. (Note that a few harmonics from five lattice rows including low-order data are insufficient.) If no other information is available, the maximum admissible value for the g's may be used: $g \leq m$. Thus, if $g_{\rm max}$ (perhaps augmented by an experimental error due to the separation process) is set equal to m, one (or perhaps more) solution(s) obtained from all five rows in a first run of the algebra program can then be least-squares refined using as parameters S, B and the coordinates. Thus, a better approximation for S and B can lead to a subsequent algebra run. In general, only one (of perhaps few initial) solution(s) will survive this iterative procedure.

(ii) Even with present-day quality of scattering intensities obtained from synchrotron radiation (Kirfel & Eichhorn, 1990), the precision of $|F_a|$ and $|F_n|$ obtained by the separation process is necessarily less than that of the original data and depends mainly on the relative dispersive contrast $|F_1|^2 - |F_2|^2/\frac{1}{2}(|F_1|^2 + |F_2|^2)$ between measurements at two X-ray energies. $\Delta f'_a$ is the only parameter that can be changed experimentally: For atoms with high order number Z, high contrast can be achieved in using L and perhaps M edges (Hendrickson, 1995). Moreover, using the absolute experimental contrast implies a relative scaling of both measurements with much better accuracy than needed for S. The method of Karle (1980), appropriate for scaling MAD data, is again based on Wilson's statistics, and may therefore be unreliable for a few data only. A possible remedy exists in energy-dispersive measurements but this still requires work on details (see *e.g.* Fischer, Krane & Morgenroth, 1996). (Other systematic errors, *e.g.* from extinction, are not considered here.)

g_h represents the structure-factor modulus of a centrosymmetric point structure, all points with unit weight, and the number of points ($2m$) being known. Consequently, the method may not work for a partial structure of atoms randomly distributed over an unknown number of sites. On the other hand, unusually small distances between atoms, be it in three-dimensional space or in the projections, do not preclude a solution. (Chemically reasonable distances should, of course, be used in discriminating against a false pseudohomometric solution.) It should be mentioned that, while ordered distribution of the a atoms is necessary, this is not a prerequisite for the n atoms: only their F_n's need to be known, not the number of n-atom positions occupied.

In mathematical terms, the algebra contains relations between harmonic g_h that can all be derived from the 'addition formulae' for cosine of multiple arguments such as

$$\cos(2x) = 2\cos^2 x - 1$$

$$\cos(3x) = 4\cos^3 x - 3\cos x$$

etc. No statistical or probability arguments are used and all equations are derived without approximation. They are related to ideas of Ott (1928), Banerjee (1933) and Avrami (1939), which could not be carried through to much practical use. Our representation of the point distribution (projected in one dimension) by m roots of the polynomial $R[\cos(2\pi x)]$ [or transformed in $R(x)$] can produce single solutions, degenerate ones or (by virtual small 'movements' of the azimuthal axis in a vertical direction, caused by errors in the g_h) double roots or doubly complex ones. This can be easily recognized and critically analysed by plotting $R(x)$. (Again, knowledge of the number m of atoms looked for is a necessary condition.)

The point tomography is executed best using three orthogonal projections (or nearly so) and 'diagonals' having about the same angles with the two main lattice lines whose parameters are to be attached to the atoms looked for. In space groups with systematic extinctions, the selection of diagonals (and sometimes of main projections, at least regarding the sequence of their treatment) deserves careful consideration.

The method is expected to work also for structures containing one type of a atom only (in this case F_n is identical with F_{nn}): Having determined the partial structure of the resonant atoms, the signs of all those $|F_n(\mathbf{h})|$ can be found whose corresponding $|F_a(\mathbf{h})|$ is sufficiently large, $s_r(\mathbf{h})$ thus being applicable with safety. [Evidently, the probability to obtain a reliably defined sign of $|F_n|$ (or $|F_{nn}|$) is higher for a structure having a_1 and a_2 compared with a structure with only one anomalous scatterer.]

Care has to be taken if an a-atom arrangement represents a substructure, with special positions leading to 'extinction rules' in addition to the general ones of the space group (for their partial structure factors only). For the class of reflections concerned, sign determination of the $|F_n|$ is impossible (as it would be with any other 'heavy atom' or similar technique).

The degree of uniqueness obtainable depends, of course, mainly on the quality of the data, judged against the amount of pseudohomometry or pseudosymmetry in the structure itself. While the latter cannot be parametrized, Bragg reflection intensities can nowadays be measured with synchrotron radiation to a precision that compares well (for medium and strong reflections) with that of the best X-ray tube data and that is superior for weak intensities (Kirfel & Eichhorn, 1990; Eichhorn, Kirfel, Grochowski & Serda, 1991). Therefore, the main errors introduced originate from the separation procedure and the scaling, all being partly systematic (see above).

We do not try to advocate this method for general use: It may be helpful in starting a structure determination safely by providing unambiguous partial structures (or if not by presenting all possible solutions for further consideration): no pseudohomometric case is left undetected by the crystallographer. Consequently, our technique might also be useful for structures that resisted a first incontestable solution by conventional methods. (In this case, the $|F|$'s are already on a nearly absolute scale.)

The sequence of steps suggested in the *Abstract* is (for space group $P\bar{1}$):

(i) Select three independent (central) reciprocal-lattice rows ('class 1'), plus two (or more) linear combinations of them ('diagonals, class 2') such that non-zero indices from all rows of class 1 are used at least once.

(ii) Measure intensities of (at least) the first $m + 1$ reflection orders for each row at three (or more) wavelengths $\lambda > \lambda_a$. Obtain $|F_a|$, $|F_n|$ and s_r for all reflections on an approximately absolute scale.

(iii) For each row (and each kind of a atom), reduce $|F_a(h)|$ to $g_{a,h}$ and apply the 'recursive algebraic technique'. (Choose a sign for $h = 1$ only at 'class 1' rows.) Calculate individual coordinate error regions by Monte Carlo techniques.

(iv) Recover the three-dimensional partial a structure by using point tomography.

(v) Find signs of F_{nn} (*via* origin alignment in the case of two kinds of a atoms) and determine the partial structure of n atoms by any suitable method.

If in steps (iii) to (v) no pseudohomometric case remains unsolved (and no homometry is encountered), the structure has been determined uniquely within the error limits.

Steps (iii) plus (iv) constitute a new technique for partial structure analysis without Fourier methods requiring few selected data only. It has almost *ab initio* character and offers high spatial resolution.

At present, our algebra program is not yet ready to allow 'black box' (routine) use for all centrosymmetric space groups. We experienced, however, no fundamental problems in working with space group *Pnma*. For the case of special positions (*e.g.* $x = 0$, $x = 1/2$ in a one-dimensional projection), a slightly modified version exists. We hope to have the program ready for distribution to interested colleagues in a short time.

This work was supported by the Deutsche Forschungsgemeinschaft (DFG) within the Schwerpunktprogramm 'Pseudosymmetrische Kristalle ...' under contract Fi107/35-2,3,4. A preliminary version of the algebraic method and a first discussion of Jagodzinski's (1971) idea were taken from the PhD thesis of Dr W. Knof (1989), which deserves our special acknowledgement. We thank Drs H.-G. Krane (Würzburg), W. Morgenroth (Hamburg) and St. Kek (Saarbrücken) for practical assistance with multi-wavelength measurements at HASYLAB (Hamburg), their data reduction and least-squares joint refinement. In particular, we thank Dr A. Pfitzner and Professor H. J. Deiseroth (Siegen) for providing the sample and their experimental results prior to publication, and Professor A. Kirfel (Würzburg, now Bonn) for critically reading the manuscript. Last but not least, we appreciate very much the constructive criticism from the Co-editor and an unknown referee, which were helpful in improving this paper.

References

Avrami, M. (1939). *Z. Kristallogr.* **100**, 381–393.

Banerjee, K. (1933). *Proc. R. Soc. London*, **141**, 188–193.

Buerger, M. J. (1959). *Vector Space and its Application in Crystal-Structure Investigation*, pp. 183 ff. New York: John Wiley.

Eichhorn, K., Kirfel, A., Grochowski, J. & Serda, P. (1991). *Acta Cryst.* B**47**, 843–848.

Fischer, K. F. (1981). *Z. Naturforsch. Teil A*, **36**, 1253–1254.

Fischer, K. F. (1987). *Z. Kristallogr.* **179**, 77–95.

Fischer, K. F., Krane, H.-G. & Morgenroth, W. H. W. (1996). *Nucl. Instrum. Methods*, A**369**, 306–311.

Fischer, K. F. & Pilz, K. (1995). ECM16, Lund, Abstract No. M07-07, 54.

Hendrickson, W. A. (1985). *Trans. Am. Crystallogr. Assoc.* **31**, 11–21.

Hendrickson, W. A. (1995). Private communication.

Jagodzinski, H. (1971). *Z. Kristallogr.* **133**, 234–241.

Karle, J. (1980). *Int. J. Quantum Chem. Symp.* **7**, 357–367.

Kirfel, A. & Eichhorn, K. (1990). *Acta Cryst.* A**46**, 271–284.

Knof, W. (1989). PhD thesis, University of Saarbrücken, Germany.

Ott, H. (1928). *Z. Kristallogr.* **66**, 136–153.

Patterson, A. L. (1939). *Nature (London)*, **143**, 939–940.

Pfitzner, A. (1995). *Z. Anorg. Allg. Chem.* **621**, 685–688.

Pilz, E. (1995). PhD thesis, University of Saarbrücken, Germany.

Pilz, K. & Fischer, K. F. (1996). *Z. Kristallogr.* Suppl. 11, p. 11.

Pilz, K. & Fischer, K. F. (1997). Submitted to *Acta Cryst.*

Pilz, K., Kek, S., Krane, H.-G., Morgenroth, W., Pfitzner, A., Adiwidjaja, G. & Fischer, K. F. (1994). HASYLAB Annual Report, pp. 465–466. HASYLAB, DESY, Hamburg, Germany.

Prandl, W. (1990). *Acta Cryst.* A**46**, 988–992.

Prandl, W. (1994). *Acta Cryst.* A**50**, 52–55.

Spilker, J. (1983). *BLFLS: Block-Diagonal and Full Matrix Least-Squares Program.* University of Saarbrücken, Germany. Unpublished