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Acta Cryst. (1990). **A46**, 681–688

Experimental Distinction of Elements with Similar Atomic Number using Anomalous Dispersion (δ Synthesis): an Application of Synchrotron Radiation in Crystal Structure Analysis

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(Received 15 June 1989; accepted 3 April 1990)

Abstract

A two-wavelength method (δ synthesis) which deals with the experimental distinction of elements with similar atomic number by means of single-crystal X-ray diffraction measurements is presented. This method uses the characteristic wavelength dependence of the anomalous-dispersion correction terms f' and f'' close to the absorption edges of the corresponding elements. In case of a properly chosen wavelength combination the resulting difference electron density map (δ map) mainly shows peaks at the positions of the 'near-edge' element. The basic mathematical formalism is described and selection rules for the determination of the optimal wavelength combination are derived. The applicability in case of mixed occupancy and/or occupancy deficiency is discussed. A series of δ maps which are based on theoretical data sets and calculated according to the formalism of the δ synthesis are shown. From this the influence of errors on the interpretation of the δ map can be estimated and the requirements on the experimental conditions can be determined. First experimental results concerning the distinction of Pb/Bi in the well known crystal structure of galenobismutite (PbBi_2S_4) are presented. They show that the δ synthesis is not only a theoretical model, but can be applied successfully in practice. For experimental reasons the applicability of the δ synthesis is restricted to elements with atomic numbers greater than $Z = 22$.

Introduction

The experimental distinction of elements with similar atomic number Z (e.g. Pb/Bi) in crystal structures

by use of conventional X-ray diffraction techniques is usually not possible due to the small difference of the corresponding atomic scattering power f_j . The only way to solve this problem is to enlarge these differences. This can be done using anomalous dispersion effects.

The atomic scattering factor f_j is usually written as

$$f_j(\mathbf{h}, \lambda) = f_j^0(\mathbf{h}) + f_j'(\lambda) + if_j''(\lambda),$$

$$f_j^0 = Z \text{ in case of } (\sin \theta)/\lambda = 0.$$

The terms f_j' and f_j'' due to anomalous scattering vary drastically only close to the absorption edges. Apart from that they are nearly wavelength independent. This physical property can be used to solve the crystallographic problem outlined above by choosing a suitable wavelength to contrast the electron density map.

However this method remained generally theoretical in the past, as long as experimental requirements such as (1) free choice of the wavelength and additionally high photon flux in the X-ray region and (2) small bandwidth (i.e. small $\Delta\lambda/\lambda$) were not available. Recently the rapid development of improved synchrotron radiation sources has made it an experimental method.

In 1984, a paper was presented (Ohsumi, Tsutsui, Takeuchi & Tokonami, 1984) in which an attempt was made to determine the Pb/Bi distribution in the crystal structure of lillianite ($3\text{PbS}\cdot\text{Bi}_2\text{S}_3$). The experiment was carried out at the Photon Factory in Japan at a wavelength close to the L_{III} absorption edge of lead. The data were analysed using the usual difference Fourier synthesis. But the atomic positions were not distinguished definitely due to insufficient

experimental conditions, namely (1) broad $\Delta\lambda/\lambda$ due to a graphite monochromator, (2) wavelength not close enough to the absorption edge, (3) too few data.

In this paper a two-wavelength method is described and experimentally verified which is much more straightforward from the theoretical point of view than single-wavelength techniques (Wulf, 1986). This method, which was first suggested by Kupčik (1979), will be referred to as δ synthesis.

Mathematical formalism of the δ synthesis

To understand the mechanism of the δ synthesis we have to recall briefly the relation between the atomic scattering factor f_j , the structure factor $F(\mathbf{h})$ and the electron density $\rho(\mathbf{r})$:

$$\begin{aligned} F(\mathbf{h}) &= \sum_j m_j f_j \exp [2\pi i(\mathbf{h} \cdot \mathbf{r}_j)] \exp [B_j(\mathbf{h})] \\ &= \sum_j m_j f_j G_j(\mathbf{h}) T_j(\mathbf{h}) \end{aligned}$$

where m_j is the occupancy factor, f_j the atomic scattering factor, $G_j(\mathbf{h})$ a geometrical term, and $T_j(\mathbf{h})$ is the Debye-Waller factor. Then

$$\begin{aligned} \rho(\mathbf{r}) &= (1/V) \sum_{\mathbf{h}} F(\mathbf{h}) \exp [-2\pi i(\mathbf{h} \cdot \mathbf{r})] \\ &= (1/V) \sum_{\mathbf{h}} \left[\sum_j m_j (f_j^0 + f_j' + if_j'') G_j(\mathbf{h}) T_j(\mathbf{h}) \right] \\ &\quad \times \exp [-2\pi i(\mathbf{h} \cdot \mathbf{r})]. \end{aligned}$$

The effect of wavelength variation on the electron density map can mathematically be conveniently described by differentiation of $\rho(\mathbf{r})$:

$$\partial\rho/\partial\lambda = (1/V) \sum_{\mathbf{h}} [\partial F(\mathbf{h})/\partial\lambda] \exp [-2\pi i(\mathbf{h} \cdot \mathbf{r})]. \quad (1)$$

The fundamental theoretical and experimental requirement of the δ synthesis is the availability of two suitable wavelengths which meet the following conditions:

$$\partial f_n/\partial\lambda = 0 \quad \text{and} \quad \partial f_e/\partial\lambda \neq 0 \quad (i)$$

where e denotes the 'edge' element, n the 'normal' scattering element.

The interpretation of the δ map is essentially simplified, if we additionally require that

$$\partial f_i''/\partial\lambda = 0 \quad \forall i \quad (ii)$$

is valid at least in a small wavelength range. Then (1) reduces to:

$$\begin{aligned} \partial\rho/\partial\lambda &= (1/V) \sum_{\mathbf{h}} \left[\sum_j m_j (\partial f_j'/\partial\lambda) G_j(\mathbf{h}) T_j(\mathbf{h}) \right] \\ &\quad \times \exp [-2\pi i(\mathbf{h} \cdot \mathbf{r})] \\ \Rightarrow \delta\rho &= (1/V) \sum_{\mathbf{h}} \left[\sum_j m_j \delta f_j' G_j(\mathbf{h}) T_j(\mathbf{h}) \right] \\ &\quad \times \exp [-2\pi i(\mathbf{h} \cdot \mathbf{r})]. \end{aligned} \quad (2)$$

It can easily be seen from (2) that the peak height in this special difference electron density map corresponds to the gradient of the real part of the anomalous-dispersion correction term. So, if a wavelength pair can be chosen such that

$$\delta f_e' \gg \delta f_n', \quad \delta f_n'' = 0, \quad (iii)$$

the δ map shows only a part of the structure, namely the positions of the 'near-edge' elements which may be regarded as 'heavy atoms'. So far, the formalism described is quite general and further procedures depend on the application under consideration. For example, these differences may be used to solve unknown crystal structures. In this case it is worth noticing that $\delta f_i' = \text{constant}$ in reciprocal space and consequently the situation is comparable to neutron scattering. Although the scattering factors derived from differences are essentially smaller it may be possible to apply the standard structure solving methods.

The aim of the δ synthesis presented in this paper is not the crystal structure determination *ab initio* but the refinement of a crystal structure with known atomic sites but unknown assignment of the elements with similar atomic number. So condition (iii) has to be modified slightly, since there is a second anomalous-scattering element in the structure, and consequently $\delta f_n'' \neq 0$. The basic idea of the δ synthesis is to use the known 'average' structure to determine the phases and signs of $\delta F(\mathbf{h})$ respectively. The expression 'average structure' means that the elements with similar atomic number are distributed statistically at the possible atomic sites. In the case of a centrosymmetric structure the δ map is calculated according to

$$\delta\rho = (1/V) \sum_{\mathbf{h}} \text{sign} [F_{\text{av}}(\mathbf{h})] \delta |F(\mathbf{h})| \exp [-2\pi i(\mathbf{h} \cdot \mathbf{r})] \quad (3)$$

with

$$\delta |F(\mathbf{h})| = |F_{\lambda_1}(\mathbf{h})| - S |F_{\lambda_2}(\mathbf{h})|$$

where $F_{\text{av}}(\mathbf{h})$ is the structure factor of the 'average' structure. The scale factor S takes into account the different experimental conditions at different wavelengths (e.g. slight change of the absorption coefficient).

This procedure is strictly valid in the case of centrosymmetric crystal structures with 'normal' distributed intensities. Then the number of reflections with wrongly determined signs will be small since a change of signs due to anomalous dispersion concerns only weak reflections. Owing to the Fourier summation this effect can be neglected. For the same reason errors due to the neglect of the small additional phase by the imaginary anomalous-dispersion term f'' are small. In the case of acentric structures the situation is somewhat more difficult and problems may occur

owing to significant phase changes. So the experimental conditions (*i.e.* the appropriate choice of the two wavelengths) have to be chosen such that the change of phases can be minimized.

Interpretation of the δ map

The applicability of the δ synthesis is clearly seen from a discussion of (2), *i.e.* the terms in brackets. Generally we may distinguish three 'basic' cases:

(1) fully occupied atomic site
 $\Rightarrow m_i = 1$, then the ratio of peak heights is $\approx \delta f'_e / \delta f'_n$, assuming that $T_e \approx T_n$;

(2) atomic site with occupancy deficiency
 $\Rightarrow m_i < 1$, and the occupancy factor m_i can be approximately estimated from the δ map by comparison with the residual electron density of a 'fully occupied' position if present in the structure;

(3) mixed occupied atomic site
 $\Rightarrow m_1 + m_2 = 1$; the peak height decreases according to the amount of the 'normal' scattering element.

Obviously, occupancy deficiency and mixed occupancy cannot be distinguished only by means of the δ synthesis. This ambiguity can be resolved by taking into account additionally the usual difference electron density map [*i.e.* $\Delta F(\mathbf{h}) = F_o(\mathbf{h}) - F_c(\mathbf{h})$] calculated from the data set obtained at a wavelength far away from the absorption edge. In the case of occupancy deficiency this density map shows a reduced electron density too - depending on the degree of occupancy - while in the case of mixed occupancy no electron deficiency occurs owing to the (nearly) equal atomic scattering power of both elements at this wavelength.

Additionally, we have to mention that in general $T_e \neq T_n$ and correspondingly the ratio of peak heights is modified by T_e/T_n . Therefore, in the case of a quantitative analysis of the δ map it is necessary to determine in a first step besides the degree of occupancy also the temperature factors using the 'reference' data set.

In the case of crystal structures more complicated than those described above (*e.g.* one atomic position occupied by more than two different kinds of atoms) a sophisticated discussion of the experimental results will be necessary but is not in general carried out here. Possibly a measurement with another wavelength could be necessary to resolve ambiguous results.

Furthermore, the problem of adequate scaling of data sets at two different wavelengths is not discussed here, but is referred to in the relevant literature (Karle, 1984).

Selection of the optimal wavelength combination

As pointed out before, the proper choice of the wavelengths is most essential for the interpretation

of the δ map. The principle of optimization is shown by means of the actual example of a Pb/Bi distribution. Fig. 1 shows a plot of the theoretical anomalous-dispersion correction terms $f'_{\text{Pb,Bi}}$ and $f''_{\text{Pb,Bi}}$ close to the L_{III} absorption edges of lead and bismuth calculated according to Cromer & Liberman (1981). It can be easily seen that the fundamental requirement of condition (i) can be fulfilled by several pairs of wavelength combinations [*e.g.* (A, B), (B, C), (C, D), (D, E), (E, F) and (F, G)]. However, if we take into account the requirement of minimization of phase changes and reduction of absorption problems in combination with condition (ii), the number of possible wavelength combinations will be drastically reduced. As a result two basic 'selection rules' are valid:

(1) $\partial f''_i / \partial \lambda \propto \partial \mu_i / \partial \lambda \approx 0 \forall i$. Then (a) the linear mass absorption coefficient μ varies only slightly with the alteration of the wavelength and consequently problems due to wrong absorption correction can be minimized; (b) the phases too change only slightly; (c) the assumption of condition (ii) is valid and consequently a simple interpretation of the δ map is possible.

(2) $\lambda_{1,2} > \lambda_{\text{edge}}$, *i.e.* the measurements should be carried out at the long-wavelength side of both absorption edges to keep the linear mass absorption coefficient as low as possible.

If we apply these 'selection rules', the optimal wavelength combination turns out to be (F, G). In the case of the distinction of lead and bismuth the wavelength combination $\lambda_1 = 0.952$ and $\lambda_2 = 0.988$ Å is recommended. From Fig. 1 it can be seen that $\partial f''_{\text{Pb,Bi}} / \partial \lambda \approx 0$ and $\partial f'_{\text{Bi}} / \partial \lambda \approx 1.5$ electrons. However, $\partial f'_{\text{Pb}} / \partial \lambda$ is very sensitive to the actual 'near-edge' wavelength setting and may vary in the range of 4–7 electrons from a small variation of λ in the vicinity of the Pb absorption edge.

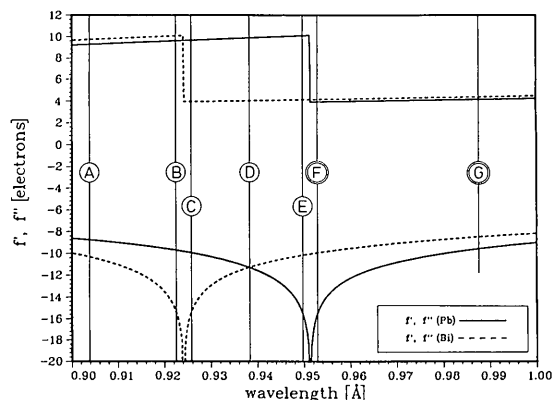


Fig. 1. Theoretical anomalous-dispersion correction terms $f'_{\text{Pb,Bi}}$ and $f''_{\text{Pb,Bi}}$ close to the L_{III} absorption edges of lead and bismuth (Cromer & Liberman, 1981). For explanation see text.

Crystal structure of galenobismutite

To verify the applicability of the δ synthesis, the well known sulfosalt galenobismutite (PbBi_2S_4 , space group $Pnma$, lattice parameters: $a_0 = 11.79$, $b_0 = 14.59$, $c_0 = 4.10$ Å) was chosen for theoretical calculations as well as for the subsequent measurements.

The structure of galenobismutite was redetermined by Iitaka & Nowacki (1962) on a natural sample by means of intensity data which were obtained from integrated equi-inclination Weissenberg photographs taken with Cu $K\alpha$ radiation. The isotropic refinement of 775 hkl data led to an unweighted R value of 9.4%. For symmetry reasons all atoms must occur on the mirror planes with z parameters at $1/4$ and $3/4$. Owing to the short c axis, reasonable interatomic distances can only be obtained with different x, y coordinates for all atoms. As a result the complete structure is seen in a projection along $[001]$. The structure consists of two crystallographically independent Bi atoms with shortest Bi-S distances of about 2.7 Å, while the Pb-S distances are 2.85 Å at least. From comparison of the MS_n polyhedra with those in known pure Pb sulfosalts the authors determined the Pb position. Fig. 2 shows a projection of the structure.

Galenobismutite seems to be ideal for several reasons:

(1) The distinction of lead and bismuth is one of the most complicated cases due to the extremely small percentage difference of the atomic scattering factors. So the theoretical and experimental results can be generalized for every other element combination.

(2) The crystal structure of galenobismutite is relatively simple. Since only the projection along the $[001]$ axis is necessary for the interpretation of the δ map, the necessary theoretical calculations are reduced.

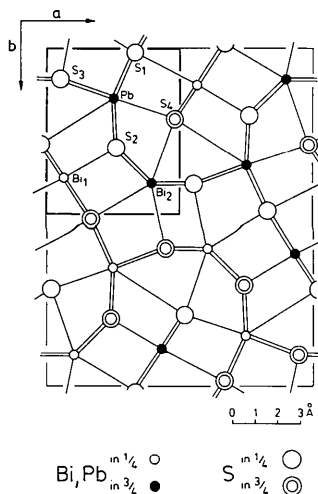


Fig. 2. Projection of the crystal structure of galenobismutite (PbBi_2S_4) along $[001]$. The asymmetric unit is bold bordered.

(3) The distribution of lead and bismuth in this structure is 'known' from crystal chemical considerations and is generally accepted.

(4) The definite distinction of Pb/Bi is of fundamental interest in sulfosalt structure analysis.

Theoretical calculations

The theoretical considerations outlined above imply error-free structure factors but do not take into account any statistical or systematic errors of the measured data (e.g. counting statistics, absorption effects). To estimate the influence of these errors on the interpretation of the δ map, a series of δ maps based on theoretical data, which have been statistically smeared by a Gaussian distribution function, was calculated. Depending on the random process, data sets with R values of 3, 6 and 9% were produced [$R = \sum (||F_o| - |F_c||) / \sum |F_o|$, F_o : structure factor after smearing of F_c].

To analyse the influence of the precise setting of the 'near-edge' wavelength different 'near-edge' wavelength settings were additionally assumed, resulting in different $\delta f'_{\text{Pb}}$ values. As can be seen from (2), the interpretation of the δ map strongly corresponds to the magnitude of $\delta f'_{\text{Pb}}$. On the other hand the 'near-edge' setting is critical from the experimental point of view, since instabilities of the synchrotron-radiation source can affect the wavelength stability. So, a compromise between stable measuring conditions and high resolution of the δ map has to be achieved.

Analysis of the δ maps resulting from the variation of $\delta f'_{\text{Pb}}$ and statistical errors gives a rough idea of the necessary experimental requirements.

The calculation of the theoretical data sets was done by means of *ORFLS* (Busing, Martin & Levy, 1962) using the atomic parameters and the Pb/Bi distribution of galenobismutite as published by Iitaka & Nowacki (1962). 345 unique $hk0$ reflections were calculated in the region of $(\sin \theta) / \lambda = 0.7$ Å⁻¹, assuming a complete ordering of Pb/Bi. The necessary anomalous-dispersion correction terms were calculated according to Cromer (1983), the atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974).

Figs. 3(a)-(c) show three typical δ maps (projections) resulting from theoretical data sets with $\delta f'_{\text{Pb}} = 6.3$ and $\delta f'_{\text{Bi}} = 1.5$ electrons respectively and various R values as described above. It can be seen that in case of $R = 0.0\%$ the ratio of peak height is approximately $\delta f'_{\text{Pb}} / \delta f'_{\text{Bi}} = 4.2$, as predicted from theory. However, in the case of R values greater than 6% the ratio of peak height no longer equals the predicted theoretical value. No doubt, the position of Pb is still recognized but a quantitative estimate of ordering is not possible.

Experimental

The experiments concerning the δ synthesis were carried out using the five-circle diffractometer at HASYLAB (Kupčik, Wulf, Wendschuh, Wolf & Pähler, 1983). The main features of this experimental setup are: (a) a four-circle diffractometer (Stoe & Cie) mounted on a fifth circle; (b) fixed exit monochromator with germanium [111] single crystals; (c) vertical beam divergence $12''$; (d) resulting wavelength resolution $\Delta\lambda/\lambda = 6 \times 10^{-4}$; (e) wavelength range $0.3\text{--}2.2 \text{ \AA}$.

According to theoretical considerations, the wavelengths were set to $\lambda_1 = 0.953$ and $\lambda_2 = 0.988 \text{ \AA}$. The precise setting of the 'near-edge' wavelength was controlled by taking a near-edge absorption spectrum of a lead-containing powder sample.

Although only $hk0$ reflections are necessary for the δ synthesis in the case of galenobismutite, two complete data sets were measured in order to estimate the quality of data obtained with synchrotron radiation.

Additionally a control measurement at a conventional X-ray tube using Mo $K\alpha$ radiation was carried out with the very same sample to separate effects due to sample properties.

The single-crystal measurements were carried out with a synthetic needle-like galenobismutite sample ($8 \times 80 \times 1200 \mu\text{m}$) with well grown crystal faces. Crystal growth was done by chemical transport reaction with iodine as transporting agent in a temperature gradient of $933/1003 \text{ (K)}$. In the region of $(\sin \theta)/\lambda \leq 0.8 \text{ \AA}^{-1}$, approximately 1400 unique reflections were measured at each wavelength in the ω step-scan mode. The intensity data were corrected for Lorentz and polarization factors. Additionally an empirical absorption correction (Sheldrick, undated; XEMP4) based on Ψ scans was carried out. Table 1 summarizes

the different experimental parameters of these three measurements as well as the results.

Experimental results

(I) Structure redetermination

The present studies, using synchrotron radiation as well as Mo $K\alpha$ radiation, lead to an unweighted R value of $\sim 10\%$. This figure of merit was significantly improved to $R = 5.35\%$ by anisotropic refinement of all atoms. This limited R value is a typical result in the case of crystal structure analysis on sulfosalts, since correct absorption correction is difficult due to (a) extremely anisotropic crystal growth (usually thin needles grown along the short c axis), in combination with (b) strong absorbing elements (Pb, Bi). Table 2* shows the resulting refined atomic parameters of galenobismutite from data at $\lambda = 0.988 \text{ \AA}$. Compared with the original structure determination the standard deviations of the atomic parameters were reduced by a factor of 3. Table 1 summarizes the experimental results. It is worth noticing that in the case of synchrotron measurement only three reflections were found to be unobserved [$F_o < 1.5\sigma(F_o)$]. On the other hand, problems occurred due to the high counting rates of strong reflections.

(II) Distinction of the M positions

(a) δ synthesis

The δ map was calculated according to (3) using 339 unique $hk0$ reflections. The scale factor S has

* Lists of structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53200 (27 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

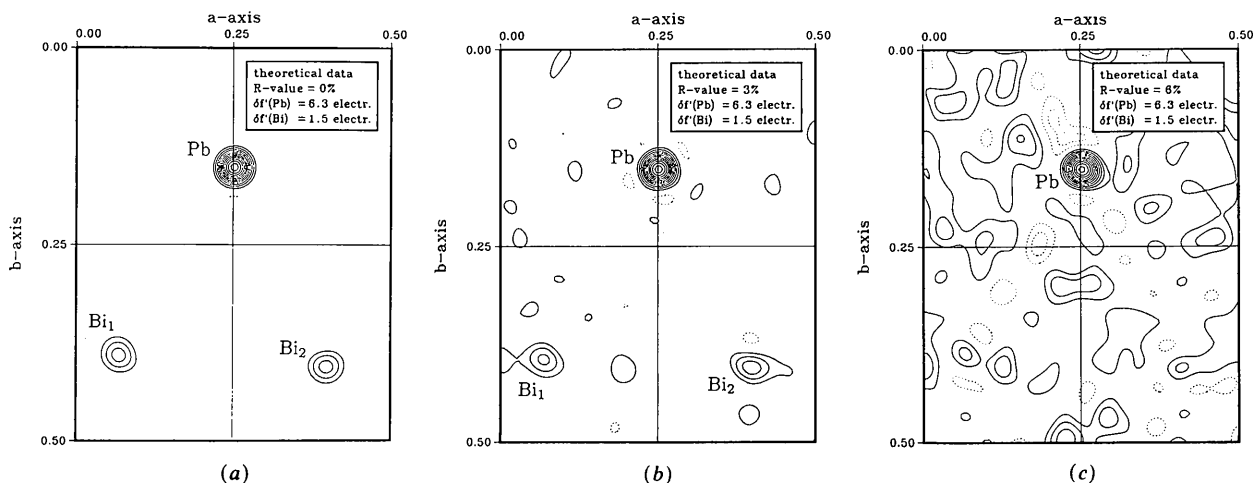


Fig. 3. Difference electron density maps (δ maps) of galenobismutite based on theoretical data sets with different statistical errors (' R value') ($\lambda_1 = 0.9528$, $\lambda_2 = 0.988 \text{ \AA}$). (a) $R = 0$, (b) $R = 3\%$, (c) $R = 6\%$. Only the asymmetric unit is shown. Projection along [001]. Contours at intervals of 5.0 e \AA^{-2} .

Table 1. Details of data-collection parameters from different measurements on galenobismutite (PbBi₂S₄)

Data collection			
Wavelength (Å)	0.7107 (Mo K α)	0.953	0.988
X-ray source	Fine focus tube	Synchrotron	Synchrotron
Instrumentation	4-circle diffractometer	HASYLAB at DESY	HASYLAB at DESY
Monochromator	Stoe Stadi 4	5-circle diffractometer	5-circle diffractometer
Degree of polarization (%)	Single crystal	Stoe Stadi 4	Stoe Stadi 4
Beam stability control	Graphite (0001)	Double crystal	Double crystal
	50	Germanium (111)	Germanium (111)
	2 standard reflections	~93	~93
		2 standard refl. +	2 standard refl. +
		real time monitorization	real time monitorization
		of polarization and beam	of polarization and beam
Time between standards (min)	120	30	30
Recording technique	ω step scan	ω step scan	ω step scan
Step width ($\Delta\omega$) (°)	0.02	0.003	0.003
Time/step (s)	0.5-2.0	0.2-2.0	0.2-2.0
Max. (sin θ)/ λ (Å ⁻¹)	0.787	0.803	0.775
Max. $h, k, l, 2\theta$ (°)	18, 22, 6, 68	18, 23, 4, 100	18, 22, 4, 100
Number of F_o 's recorded	3501	3186	2473
Unique reflections	1604	1496	1379
Data reduction			
Lp correction	Yes	Yes	Yes
Absorption correction	Ψ scans	Ψ scans	Ψ scans
Absorption coefficient μ (cm ⁻¹)	717.81	399.30	440.4
Min./max. transmission	0.116/0.801	0.208/0.592	0.208/0.592
Merging R before/after correction	0.372/0.105	0.247/0.140	0.247/0.140
Structure refinement			
Atomic scattering curves			
f_o (neutral Pb, Bi, S)	International Tables (1968)	International Tables (1968)	International Tables (1968)
f', f''	Cromer (1983)	Cromer (1983)	Cromer (1983)
Weighting scheme	$w = 1/\sigma^2$	$w = 1/\sigma^2$	$w = 1/\sigma^2$
Number of F_o 's used	1599	1496	1379
$F_o > 1.5\sigma(F_o)$	1488	1496	1376
$R_{int} = \sum F^2 - F_{mean}^2 / \sum F^2$ (%)	2.81	3.54	3.0
$R = \sum F_o - F_c / \sum F_o $ (%)	5.69	5.35	5.65

Table 2. Final fractional atomic coordinates and anisotropic thermal parameters U_{ij} (Å²) of galenobismutite (PbBi₂S₄) from synchrotron data ($\lambda = 0.988$ Å)

$$T_{hkl} = \exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^*)].$$

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}
Bi(1)	0.06818 (3)	0.39055 (3)	0.25	0.0138 (3)	0.0128 (3)	0.0142 (5)	0.0011 (1)
Bi(2)	0.10173 (3)	0.90535 (3)	0.25	0.0186 (3)	0.0220 (3)	0.0123 (5)	0.0003 (1)
Pb(1)	0.24675 (3)	0.65234 (3)	0.25	0.0269 (3)	0.0196 (3)	0.0192 (5)	0.0032 (1)
S(1)	0.33396 (17)	0.01487 (13)	0.25	0.0185 (7)	0.0145 (7)	0.0205 (13)	0.0013 (3)
S(2)	0.25944 (15)	0.29707 (13)	0.25	0.0126 (7)	0.0139 (7)	0.0133 (10)	0.0003 (3)
S(3)	0.05470 (17)	0.09252 (15)	0.25	0.0158 (7)	0.0113 (7)	0.0198 (12)	0.0002 (3)
S(4)	0.01839 (15)	0.71166 (13)	0.25	0.0137 (6)	0.0115 (7)	0.0130 (10)	0.0000 (3)

been determined by successive smoothing of the δ map. In this way S was found to be 1.05. Fig. 4 shows the resulting two-dimensional δ map of galenobismutite resulting from experimental data.

The very low background of the experimental δ map shows that the 'internal consistency' of the data is much better than would be expected from the R value. From comparison with Figs. 3(b) and (c) a figure of merit $\approx 3\%$ can be estimated. This corresponds to the internal R value obtained from equivalent reflections (see Table 1). This indicates that the δ synthesis seems to be insensitive to certain systematic errors which strongly affect the R value, since both data sets are affected in the same way.

The atomic positions of lead and bismuth can be distinguished without ambiguity. However, the quan-

titative interpretation of this map, *i.e.* the determination of m_j , is difficult for several reasons:

(1) f'_{Pb} is not known exactly close to the absorption edge of lead, since the theoretical values according to Cromer are incorrect, and the wavelength setting was not on an absolute scale;

(2) the scale factor is not known from 'objective' criteria;

(3) $T_{Pb} \neq T_{Bi}$.

From (2), (3) it is seen that besides m_j just these parameters determine the ratio of peak height. To deconvolute these parameters, in a first step the data set at $\lambda = 0.988$ Å was used to determine the temperature and occupancy factor by least-squares refinement techniques. At this wavelength $f_{Pb} \approx f_{Bi}$ is valid and consequently no problems occur from

wrong assignment of the M positions. In the second step, the parameters derived were used for the subsequent calculations, assumed to be independent of wavelength.

In this way, a theoretical δ synthesis was calculated using $f'_{\text{Pb}} = -14.8$ electrons (*i.e.* $\delta f'_{\text{Pb}} = 5.1$), estimated from the experimental wavelength setting. It can be seen from Fig. 5 that the resulting δ map is in good agreement with the experimental one, *i.e.* galenobismutite may be regarded as a compound with complete ordering of lead and bismuth.

(b) 'Bichromatic' least-squares refinement of f'_M

A refinement of f'_M was carried out using the data set at 0.953 \AA , starting with $f'_M = -9.00$ electrons for all M positions. The positional and thermal param-

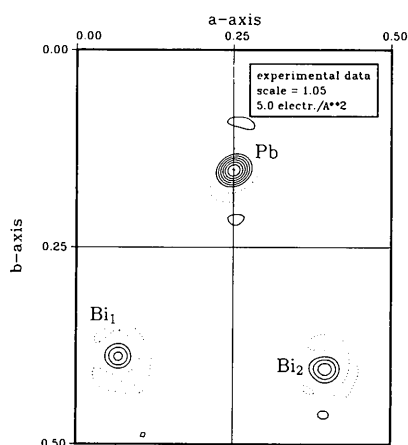


Fig. 4. Difference electron density map (δ map) of galenobismutite based on experimental data at $\lambda_1 = 0.953$ and $\lambda_2 = 0.988 \text{ \AA}$. Projection along $[001]$. Contours at intervals of 5.0 e \AA^{-2} .

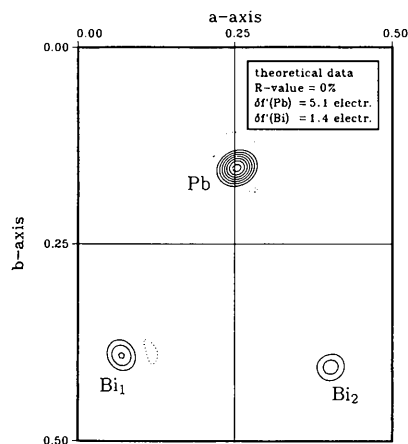


Fig. 5. Difference electron density map (δ map) of galenobismutite based on theoretical data sets, using x , y and T parameters from least-squares refinement at $\lambda = 0.988 \text{ \AA}$. $\delta f'_{\text{Pb}}$ is estimated from the experimental wavelength setting. Only the asymmetric unit is shown. Projection along $[001]$. Contours at intervals of 5.0 e \AA^{-2} .

eters were taken from the refinement of the reference data set at $\lambda = 0.988 \text{ \AA}$ and kept fixed. This 'bichromatic' refinement technique (Wulf, 1986) resulted in $f'_{M_1} = -10.1$ (2), $f'_{M_2} = -10.8$ (2) and $f'_{M_3} = -14.6$ (2) electrons. The comparison with the theoretical expected values ($f'_{\text{Pb}} \approx -14.8$ and $f'_{\text{Bi}} \approx -9.9$ electrons) definitely locates the Pb position. From this also a complete ordering can be assumed.

(c) 'Classical' refinement techniques

However, if we do not use the information involved in the reference data set at 0.988 \AA and refer only to a single near-edge measurement, the interpretation of the results is not as clear.

(1) If we refine f'_M and T , x , y of all atoms simultaneously starting from the known model, we obtain $f'_{M_1} = -7.6$ (4), $f'_{M_2} = -9.1$ (4) and $f'_{M_3} = -12.4$ (4). Although we still may locate the Pb position, the absolute values of f'_M are too low, which is compensated by the corresponding temperature factors. The interpretation of these f'_M values leads to a wrong determination of occupancy factors and M ordering respectively.

(2) Finally an attempt was made to determine the true Pb position by refinement of the three possible cation distributions. In this case $f'_{\text{Pb}} = -14.8$ and $f'_{\text{Bi}} = -9.87$ was assumed and kept fixed. The different models lead to R values of 5.35, 6.74 and 7.50%, respectively. The best R value corresponds to the Pb/Bi distribution as derived from the other methods. A significance test according to Hamilton (1965) led to $\mathcal{R}_{43,1443,0.01} = 1.032$.

Concluding remarks

The experimental results on galenobismutite show that the δ synthesis is not only a mathematical model, but can be applied experimentally. From the experimental point of view this method is somewhat sophisticated, since measurements have to be carried out at two different wavelengths. In the case of simple crystal structures such as galenobismutite, comparable results may be obtained by a single 'near-edge' measurement and analysis of the conventional difference electron density map ($\Delta F = F_o - F_c$) and least-squares refinement. But the analysis of these data may be difficult and ambiguous due to the strong correlation of T_j , m_j and f'_j .

Therefore a second data set at a 'reference' wavelength is advantageous, and in the case of crystal structures with mixed occupancy and/or occupancy deficiency even necessary to separate these correlations. On the basis of the parameters derived from this data set, a subsequent least-squares refinement of f'_j using the 'near-edge' data may also yield reasonable results. However, the δ synthesis seems to be superior even to this method, since it is based on differences. In a sense the δ synthesis may be

compared with compensation measuring techniques in physics. This way unimportant information will be eliminated while the significance of the information in question will be essentially improved. Additionally this method seems not to be sensitive to systematic errors, since both data sets are affected in the same way. The great advantage of the δ synthesis will be clearly seen in the case of more complex crystal structures than galenobismutite.

For a quantitative application in the case of occupancy deficiency and/or mixed occupancy a better knowledge of the anomalous-dispersion correction terms is necessary. Close to the absorption edges, the theoretical data according to Cromer & Liberman (1981) and Cromer (1983) are obviously incorrect, since these values do not take into account the complicated near-edge structure.

Since the distinction of lead and bismuth is an extreme example considering the small percentage difference of the atomic scattering powers, the results may be generalized for every combination of elements with similar scattering power.

The general applicability of the δ synthesis will be restricted by the limited wavelength range of the monochromators (0.3–2.2 Å). As a result, the δ synthesis can be applied for elements with an atomic number of $Z > 22$. The method can be extended to elements with a lower atomic number by use of vacuum techniques, which reduce significantly the absorption of soft X-rays by air. In this way measurements up to $\lambda \approx 7$ Å are possible (e.g. $Z_{\text{Si}} = 13 \Rightarrow \lambda_{\text{K}} = 6.7$ Å). However, the volume of the Ewald sphere decreases proportionally and the interpretation of the δ map may fail because only a small number of data is available. In the case of a typical orthorhombic silicate structure with lattice constants of $\sim 10 \times 10 \times 10$ Å, only 12 unique reflections can be measured in the range of $2\theta = 110^\circ$. Additionally, the resolution of the electron density map will be too low ($d_{\text{min}} \geq 4.09$ Å).

Nevertheless, even under the 'standard' experimental conditions a wide range of elements is covered by the δ synthesis. So this method can be applied advantageously in the scientific field of systematic structure analysis.

The author is greatly indebted to Professor Dr V. Kupčik, who initiated the present investigation, for numerous valuable discussions. Special gratitude is owed to Dipl.Min. M. Wendschuh-Josties for computational and experimental support. Thanks are also due to Professor Dr K. Bente for kindly providing the synthetic sample of galenobismutite and Professor Dr P. Süsse for reading the manuscript. The computations were carried out at the facilities of the Gesellschaft für wissenschaftliche Datenverarbeitung (GWDG) in Göttingen. This work was supported by a grant of the Bundesminister für Forschung und Technologie (BMFT) under contract no. 05 320IA B8.

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Acta Cryst. (1990). **A46**, 688–692

On the Construction of Karle–Hauptman Matrices

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(Received 4 January 1990; accepted 6 April 1990)

Abstract

The construction of a Karle–Hauptman matrix or a series of these matrices, suitable for the *ab initio* determination of phases, is presented. An algorithm

is proposed which is suggested by graph theory. Maximization of the determinant of Karle–Hauptman matrices, constructed using the new algorithm, as a function of the phases yields phase sets with very low errors compared with earlier results.