

We first solve equations (28) and (29) for ε and $(1/D)+F_1(\alpha)$. The value of ε is then substituted in equations (26) and (27) to yield estimates of $(1/D)+F_2(\alpha)$ and $(1/D)+F_3(\alpha)$. Eliminating $(1/D)$ from each of the two pairs of equations, we can evaluate two independent combinations of $F_1(\alpha)$, $F_2(\alpha)$ and $F_3(\alpha)$, say $F_1(\alpha)-F_2(\alpha)$ and $F_2(\alpha)-F_3(\alpha)$. These could then be utilized along with estimates of three other compound fault parameters obtained from other measurements, say profile peak shift and profile asymmetry for the $10\bar{1}4$, $10\bar{1}5$ and $10\bar{1}7$ reflexions to enable a complete evaluation of the fault probabilities to be made.

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A Method of Determining the Distortion of Coordination Polyhedra

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The distortion of an observed coordination polyhedron can be evaluated from a comparison of this polyhedron with the least-squares best-fit polyhedron with optimum location, orientation, size parameters and prescribed symmetry. A set of atoms at positions, $\mathbf{x}(1), \dots, \mathbf{x}(n)$, may be fitted to the set $\mathbf{y}(1), \dots, \mathbf{y}(n)$ by rearranging the matrix equations:

$$\mathbf{y}(i) = \mathbf{t} + R\lambda(i)\mathbf{x}(i) \quad (i = 1, n)$$

and solving for the unknown parameters of the translation vector, \mathbf{t} , the rotation matrix, R , and the (diagonal) dilation matrices, $\lambda(i)$, which optimize the fit between the two sets. The elements of the (one or more) dilation matrices may be constrained to fix the fitted set to the desired symmetry. The solution is effected by means of a two-stage iterative least-squares technique employing the so-called 'small-angle' rotation matrix. The average distance between corresponding atoms of the two sets, which is a minimum at the point of optimum fit, provides a unique one-parameter characterization of the degree of distortion between the two configurations. The magnitudes of the operations needed to produce the best fit are also recoverable from the least-squares solution.

Introduction

Coordination polyhedra observed in crystal structures are, more often than not, distorted to some degree from their ideal configurations. The extent of this distortion is a significant crystal chemical parameter. It is, however, difficult to determine quantitatively. Several methods of characterizing such distortion have been suggested (see, e.g., Robinson, Gibbs & Ribbe, 1971) and, in general, are measures of the spread of

interatomic distances or angles about their means or ideal values. Undoubtedly such variation in bond length and angles does increase from undistorted to more distorted polyhedra. It is, however, not uncommon to encounter real polyhedra, which are distorted from some ideal configuration, but yet have all bond lengths equal or all bond angles equal to those of the ideal configuration. Furthermore, it may be desirable to know the degree of distortion relative to a lower symmetry subgroup of the ideal configuration,

e.g., how closely does an observed polyhedron conform to a trigonally distorted octahedron? Lastly, the coordinates (fractional or Cartesian) of the optimum fitted set are useful in examining the distortion.

In comparing the coordinates of one set of points with another, the first may be held fixed and the second set 'adjusted' to optimize the fit. The 'adjustments' that must be considered are (rigid) rotation of the entire set and (rigid) translation of the entire set. A combination of these two operations is sufficient to bring identical sets into coincidence and similar sets into an optimum fit. In some cases it is advantageous to consider in addition the operation of dilation. If an ideal tetrahedron is to be fitted to any observed pseudotetrahedron, the question arises, what size should the ideal tetrahedron be? By choosing the size so as to optimize the fit between the two sets, the operation of dilation is introduced. In general, different dilation coefficients may be applied to different groups of atoms. For example, it is necessary to use two independent dilation coefficients in determining the best fit of a trigonal dipyramid to an observed fivefold coordination polyhedron – one dilation coefficient for the three equatorial atoms and a second for the two axial atoms of the group. As discussed in more detail below, it is sometimes necessary in fitting lower-symmetry polyhedra to employ anisotropic dilation, where, for example, the *x*- and *y*-axis coordinates are dilated independently of the *z*-axis coordinates. Thus the problem of fitting one set to another leads to a search for the translation, rotation, and dilation operations which, when applied to one set, optimize its fit with the other.

Mathematical methods

The Cartesian coordinates of the *n* vertices of the two polyhedra, $\mathbf{y}(i)$ and $\mathbf{x}(i)$, $i = 1, n$, define the two vector sets \mathbf{Y} and \mathbf{X} . Let \mathbf{Y} remain fixed and let \mathbf{X}^j be the vector set (the right superscript identifies the iteration cycle) produced from the original set, \mathbf{X}^0 , by the operations of translation, rotation, and dilation:

$$\mathbf{x}^j(i) = \mathbf{t} + R\lambda(i)\mathbf{x}^0(i), \quad i = 1, n, \quad (1)$$

where \mathbf{t} represents the translation vector, R is the rotation matrix and $\lambda(i)$ is the dilation matrix applied to the *i*th vector. The elements of these matrices are:

$$R = \begin{pmatrix} l^2 + (1-l^2)\cos\theta & lm(1-\cos\theta) - n\sin\theta & ln(1-\cos\theta) + m\sin\theta \\ ml(1-\cos\theta) + n\sin\theta & m^2 + (1-m^2)\cos\theta & mn(1-\cos\theta) - l\sin\theta \\ nl(1-\cos\theta) - m\sin\theta & nm(1-\cos\theta) + l\sin\theta & n^2 + (1-n^2)\cos\theta \end{pmatrix}$$

for a counterclockwise rotation of θ around an axis with direction cosines, l, m, n . In the most general case the dilation matrices have the diagonal form,

$$\lambda(i) = \begin{pmatrix} d_1 & 0 & 0 \\ 0 & d_2 & 0 \\ 0 & 0 & d_3 \end{pmatrix}$$

where d_j are independent (anisotropic) dilation coefficients. If the vectors, $\mathbf{x}(a)$ and $\mathbf{x}(b)$ are symmetry equivalent then $\lambda(a) = \lambda(b)$, *etc.*

Let $u(i)$ be defined as the vector separating the *i*th vector of the fixed set and the corresponding vector of the rotated set, *i.e.*:

$$\mathbf{u}(i) = \mathbf{y}(i) - \mathbf{x}^j(i). \quad (2)$$

A measure of the goodness-of-fit between sets, \mathbf{Y} and \mathbf{X}^j , is then given by U ,

$$U = \sum_{i=1}^n [\mathbf{u}(i)]^2. \quad (3)$$

If the operations, t , R and λ are chosen to minimize U , the resulting translated-rotated-dilated set, \mathbf{X}^j , may be said to be 'best-fit' to the set, \mathbf{Y} , in a least-squares sense. These desired values of t , R , and λ may be determined through the rearrangement and (non-linear) least-squares solution of equations:

$$\mathbf{y}(i) = \mathbf{t} + R\lambda(i)\mathbf{x}^0(i), \quad i = 1, n. \quad (4)$$

The translation component, \mathbf{t} , may be easily eliminated. Equation (3) may be expanded:

$$U = \sum_{i=1}^n \{\mathbf{y}(i) - [\mathbf{t} + R\lambda(i)\mathbf{x}^0(i)]\}^2. \quad (5)$$

The value of \mathbf{t} which will minimize U is evidently given by differentiating U with respect to \mathbf{t} and setting this expression equal to zero:

$$\sum_{i=1}^n -2[\mathbf{y}(i) - R\lambda(i)\mathbf{x}^0(i) - \mathbf{t}] = 0. \quad (6)$$

Rearranging gives:

$$\mathbf{t} = \frac{1}{n} \sum_{i=1}^n \mathbf{y}(i) - \frac{1}{n} \sum_{i=1}^n R\lambda(i)\mathbf{x}^0(i). \quad (7)$$

That is, \mathbf{t} is merely the translation vector that relates the centroids of the two sets, and if \mathbf{Y} and \mathbf{X}^0 are so chosen that the centroids of \mathbf{Y} and $R\lambda(i)\mathbf{X}^0$ are at the origin of coordinates, then \mathbf{t} vanishes, and equation (4) reduces to

$$\mathbf{y}(i) = R\lambda(i)\mathbf{x}^0(i), \quad i = 1, n, \quad (8)$$

where \mathbf{Y} and \mathbf{X}^0 are centered sets.

After elimination of \mathbf{t} , the remaining variables R and $\lambda(i)$ may be determined, in the most general case, by a two-step iterative least-squares procedure. The solution makes use of an approximation of the rotation matrix, called the small-angle or infinitesimal rotation matrix (see, *e.g.*, Thompson, 1969). If the rotation

angle, θ , is small then, $\cos \theta \approx 1$ and the R matrix given above can be approximated by the matrix:

$$S = \begin{pmatrix} 1 & -n\theta & m\theta \\ n\theta & 1 & -l\theta \\ -m\theta & l\theta & 1 \end{pmatrix}.$$

Stage 1: The (diagonal) components of the dilation matrices are set to unity and the true rotation matrix R is replaced by the approximation S , whereby equation (8) can be rewritten:

$$y(i) = Sx^0(i), \quad i = 1, n. \quad (9)$$

These equations are linear in the components of S (which is not the case for R) and may be rearranged in the matrix form $Y = CP$ with matrix elements:

$$\begin{bmatrix} \cdot \\ \cdot \\ \cdot \\ y_{i1} - x_{i1} \\ y_{i2} - x_{i2} \\ y_{i3} - x_{i3} \\ \cdot \\ \cdot \\ \cdot \end{bmatrix} = \begin{bmatrix} \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot \\ 0 & x_{i3} & -x_{i2} \\ -x_{i3} & 0 & x_{i1} \\ x_{i2} & -x_{i1} & 0 \\ \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot \end{bmatrix} \begin{bmatrix} l\theta \\ m\theta \\ n\theta \end{bmatrix}. \quad (10)$$

This matrix equation is solved by the usual least-squares methods for an estimate of the parameter matrix:

$$P = (\tilde{C}C)^{-1} \tilde{C}Y \quad (11)$$

where the tilde represents the transposed matrix. The rotation parameters may then be separated:

$$\theta = \{ (l\theta)^2 + (m\theta)^2 + (n\theta)^2 \}^{1/2}, \quad \text{and} \quad l = (l\theta)/\theta, \text{ etc.}$$

These parameters are used to construct the first estimate of the rotation matrix, R .

Stage 2: Employing the R matrix determined in the first stage, equation (8) can be rearranged to a set of equations, again in matrix form $Y = CP$,

for an example with two different anisotropic dilation matrices. These equations are solved by least-squares methods to give first estimates of the dilation matrix elements which, in turn, are used to construct the better fitted set:

$$x^1(i) = R\lambda(i)x^0(i), \quad i = 1, n. \quad (13)$$

The next iteration is begun by replacing X^0 in equation (8) by the set X^1 (recentered, if necessary) proceeding as above, which yields a new rotation matrix and new dilation matrix elements. These new operations may then be applied to set X^1 to give an even better fit set X^2 , analogous to equation (13). Conversely an overall rotation can be formed from the product of the rotation matrices determined in the first and second iterations and, similarly, overall dilation matrices can be constructed from the products of the individual elements determined in the two cycles. The set X^2 can then be constructed directly from the starting set X^0 from equations of the form (13) where the operations now refer to overall operations.

Now, X^2 is a better estimate of the desired best-fit set than was X^1 . This process is reiterated until the differences between the sets X^m and X^{m-1} are sufficiently near zero. At this point then no further translation, rotation, or dilation of the set X^m will decrease U and, therefore, X^m is the desired 'best-fit' set.

The degree of fit is given directly by U , or by a more easily visualized parameter, ϵ , the r.m.s. average separation of equivalent points in Y and X^m ,

$$\epsilon = \sqrt{\bar{U}/n}. \quad (14)$$

ϵ , then is a unique one-parameter characterization of the degree of distortion of the given polyhedron, Y , from the fitted polyhedron, X^m . If X^m is an ideal polyhedron, then ϵ increases from zero as the degree of distortion increases. The exact nature or geometry of the distortion can be found from a point by point comparison of Y and X^m . The rotation parameters may be obtained from the elements of the overall rotation matrix,

$$\theta = \arccos \left(\frac{tr - 1}{2} \right) \quad \text{where} \quad tr = r_{11} + r_{22} + r_{33}$$

$$\begin{bmatrix} \cdot \\ \cdot \\ \cdot \\ y_{i1} \\ y_{i2} \\ y_{i3} \\ \cdot \\ \cdot \\ \cdot \\ y_{j1} \\ y_{j2} \\ y_{j3} \\ \cdot \\ \cdot \\ \cdot \end{bmatrix} = \begin{bmatrix} \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot \\ r_{11}x_{i1} & r_{12}x_{i2} & r_{13}x_{i3} & 0 & 0 & 0 \\ r_{21}x_{i1} & r_{22}x_{i2} & r_{23}x_{i3} & 0 & 0 & 0 \\ r_{31}x_{i1} & r_{32}x_{i2} & r_{33}x_{i3} & 0 & 0 & 0 \\ \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot \\ 0 & 0 & 0 & r_{11}x_{j1} & r_{12}x_{j2} & r_{13}x_{j3} \\ 0 & 0 & 0 & r_{21}x_{j1} & r_{22}x_{j2} & r_{23}x_{j3} \\ 0 & 0 & 0 & r_{31}x_{j1} & r_{32}x_{j2} & r_{33}x_{j3} \\ \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot \end{bmatrix} \begin{bmatrix} \cdot \\ \cdot \\ \cdot \\ \lambda_{i1} \\ \lambda_{i2} \\ \lambda_{i3} \\ \cdot \\ \cdot \\ \cdot \\ \lambda_{j1} \\ \lambda_{j2} \\ \lambda_{j3} \\ \cdot \\ \cdot \\ \cdot \end{bmatrix} \quad (12)$$

and the direction cosines are given by

$$\begin{aligned} l &= (r_{32} - r_{23})/2 \sin \theta \\ m &= (r_{13} - r_{31})/2 \sin \theta \\ n &= (r_{21} - r_{12})/2 \sin \theta. \end{aligned}$$

Applications

A computer program has been FORTRAN-coded to perform these calculations. Polyhedra consisting of up to 33 atoms can be fitted. The coordinates of an ideal polyhedron may be furnished in any convenient orientation which yields simple, Cartesian coordinates. For example, the starting coordinates of a tetrahedron could be given as: $\bar{1}\bar{1}\bar{1}$; $1\bar{1}\bar{1}$; $\bar{1}1\bar{1}$; $1\bar{1}1$, even though these may be far from the (Cartesian) coordinates of the real pseudo-tetrahedron. Conversion is surprisingly fast. With starting orientations of less than 90° away from final orientations, conversion occurs within about four to six iterations. The iterations stop when, simultaneously, rotational changes are less than 5×10^{-5} radians and dilation coefficient changes are less than 5×10^{-5} . Some of the applications where this polyhedron-fitting concept has proven to be useful may be given.

No dilation

If dilation is excluded as an operation, the procedure reduces to finding the rotation (and translation) which optimize the fit between two polyhedra. For this special case, the routine can be simplified and reduced to a simple stage iteration, or alternatively, the method given by McLachlan (1972) may be employed. The program has been used, for example, to show the pattern (amount of rotation and orientation of rotation axes) of key polyhedra in the change of the epidote structure with composition (Dollase, 1971).

Isotropic dilation

If the best fitted set can be produced by (translation), rotation, and simple radial dilation of a starting model set, then only isotropic dilation need be considered. In this case the dilation matrices reduce to scalar dilation coefficients (one for each of the symmetry-inequivalent sets of vectors), and the fitting routine can be reduced to a single-stage iteration. Examples of such cases would be the fitting of any isometric symmetry polyhedron (e.g., regular $m\bar{3}m$ octahedron or $\bar{4}3m$ tetrahedron), or in general any polyhedron in which the angular relationships about the origin are fixed by symmetry, e.g., a fivefold coordinated trigonal dipyramid (two inequivalent vector sets).

Table 1 is a compilation of the results of fitting a seven-atom ideal $m\bar{3}m$ octahedron (central atom and six ligands) to various 'distorted octahedra' whose parameters have been determined in X-ray diffraction studies found in the literature. Two points are worthy of note. First of all, the degree of distortion, in either relative or absolute terms, increases from relatively weakly distorted octahedra about Ti^{+4} in sphene through increasingly distorted octahedra about Fe^{+3} to, often very distorted, octahedral coordination about Ca^{+2} atoms. The second interesting point is that the metal-ligand distance in the best-fit octahedron is always smaller than the average M-L distance of the observed distorted octahedron. For specific symmetry cases it can be shown that this relationship must hold, but a general proof is not evident. Comparison of the volume of the observed and best-fit sets (for sets of suitable shape to have a well-defined volume) shows that the volumes are also not exactly equal. For example, the volume of the observed M(1) octahedron in olivine (see Table 2) is 12.25 \AA^3 , whereas, the volume of the best-fit $m\bar{3}m$ octahedron is 12.55 \AA^3 .

Table 1. Degree of distortion of observed pseudo-octahedra from best-fit $m\bar{3}m$ octahedra

Compound	Site	Observed M-O	Fitted M-O	Absolute distortion*	Relative distortion†
Sphene	Ti^{+4}	1.958 Å	1.958 Å	0.066 Å	3.4 %
Roemerite	Fe^{+3}	2.001	1.998	0.078	3.9
$\text{LiFeSi}_2\text{O}_6$	Fe^{+3}	2.031	2.022	0.126	6.2
Pharmacosiderite	Fe^{+3}	1.990	1.972	0.128	6.5
Acmite	Fe^{+3}	2.025	2.013	0.153	7.6
Hematite	Fe^{+3}	2.031	2.007	0.154	7.7
Epidote	Fe^{+3}	2.050	2.035	0.209	10.3
Dolomite	Ca^{+2}	2.413	2.413	0.053	2.2
$\text{CaNa}(\text{H}_2\text{PO}_2)_3$	Ca^{+2}	2.320	2.312	0.157	6.8
Pectolite	$\text{Ca}^{+2}(1)$	2.368	2.351	0.230	9.8
	$\text{Ca}^{+2}(2)$	2.360	2.340	0.223	9.5
$\text{Ca}(\text{OH})_2$	Ca^{+2}	2.366	2.352	0.240	10.2
Ca_2SiO_4	$\text{Ca}^{+2}(1)$	2.375	2.345	0.352	15.0
	$\text{Ca}^{+2}(2)$	2.414	2.358	0.408	17.3
Ca-chondrodite	$\text{Ca}^{+2}(1)$	2.385	2.347	0.395	16.9
	$\text{Ca}^{+2}(2)$	2.390	2.345	0.371	15.8
	$\text{Ca}^{+2}(3)$	2.364	2.329	0.344	14.8

* R.m.s. deviation between fitted and observed sets.

† R.m.s. deviation/ (fitted M-O).

Table 2. *Least-square fit of various symmetry polyhedra to the M(1) and M(2) pseudo-octahedra observed in olivine*

	Symmetry	Fitted $\overline{M-O}$	Absolute distortion*	Relative distortion†
M(1)	$m3m$	2.112	0.248 Å	11.7%
	4 mmm	2.112	0.248	11.7
	4 mmm	2.112	0.246	11.6
	4 mmm	2.112	0.246	11.6
	$\overline{3} 2/m$	2.123	0.145	6.8
	$\overline{3} 2/m$	2.115	0.220	10.4
	$\overline{3} 2/m$	2.118	0.195	9.2
	$\overline{3} 2/m$	2.113	0.239	11.3
	$\overline{1}$	2.128	0	0
M(2)	$m3m$	2.124	0.243	11.5%
	4 mmm	2.124	0.243	11.4
	4 mmm	2.124	0.243	11.4
	4 mmm	2.124	0.243	11.4
	$\overline{3} 2/m$	2.124	0.243	11.4
	$\overline{3} 2/m$	2.125	0.230	10.9
	$\overline{3} 2/m$	2.124	0.243	11.4
	$\overline{3} 2/m$	2.125	0.234	11.0
	m	2.153	0	0

* R.m.s. deviation between sets.

† R.m.s. deviation / $\overline{M-O}$.

Anisotropic dilation

Suppose it is desired to know (*e.g.*, in interpreting spectra) whether a given distorted octahedron more nearly conforms to a trigonally distorted octahedron, or a tetragonally distorted octahedron. To answer this, the best-fit sets with symmetry $\overline{3}2/m$ and $4mmm$ respectively must be found. In the first case, isotropic dilation is insufficient as the central angles are variable, and anisotropic dilation must be employed. For the example given, if the $\overline{3}$ axis of the starting model is z , then there are two dilation coefficients to be determined (for each equivalent group of vectors), namely one coefficient to be applied to both the x - and y -axis coordinates and a second independent coefficient to be applied to the z -axis coordinates.

Table 2 gives the results of fitting octahedra with symmetry $m3m$, $\overline{3}2/m$ and $4mmm$ to the M(1) and M(2) distorted octahedra found in olivine (Birle, Gibbs, Moore & Smith, 1968). As an ideal octahedron has four trigonal axes, there are four different ways of fitting a $\overline{3}2/m$ distorted octahedron. Similarly there are three different $4mmm$ distorted octahedra. Because of the site symmetries ($\overline{1}$ and m , respectively) some of the cases are equivalent. In answer to the above question it can be seen from Table 2 that the M(2) octahedron does not approximate either simple distortion model, whereas the M(1) polyhedron can be relatively closely fitted by a trigonally distorted octahedron with O-M(1)-O angles of 81.4° .

Weighted fits

In the above, all fitting has been done with equal weights. Alternatively, the individual mismatches between the observed and fitted sets could be separately

weighted. For example, it might be desired to know the best-fitted $m3m$ octahedron with weights proportional to the atomic mass of each of the atoms. As a final example, consider the problem of fitting a square planar coordination group to the distorted CuO_4 group in CuO (Åsbrink & Norrby, 1970), where the weights of each equation are determined by the estimated standard errors of the atomic parameters, $\omega_{(i,j)} = \sigma_{(i,j)}^{-2}$.

Table 3 compares the (fractional) coordinates of the observed and weighted, best-fit square planar groups in CuO. Owing to special positions some of the atomic coordinates are constrained, resulting formally in infinite weights. The problem is circumvented computationally by using, for these coordinates, weights of 1×10^{12} , which insures that the fitted-set atoms also occupy the appropriate special positions (see *e.g.*, Table 3). The sum of the coordinate deviations, each divided by the appropriate estimated standard errors, is a measure of the statistical significance of the deviation between the fitted and observed sets.

Table 3. *Comparison of fractional coordinates of observed CuO_4 and weighted best-fit square planar CuO_4 groups in CuO*

	x	y	z
Cu	$\frac{1}{2}$	$\frac{1}{2}$	0
	$(\frac{1}{2})^*$	$(\frac{1}{2})$	(0)
O	0	0.4184 (13)	$\frac{1}{2}$
	(0)	(0.3273)	$(\frac{1}{2})$
O	$\frac{1}{2}$	-0.0816 (13)	$\frac{1}{2}$
	$(\frac{1}{2})$	(-0.0515)	$(\frac{1}{2})$
O	0	0.5816 (13)	$-\frac{1}{2}$
	(0)	(0.5515)	$(-\frac{1}{2})$
O	$\frac{1}{2}$	0.0816 (13)	$-\frac{1}{2}$
	$(\frac{1}{2})$	(0.1727)	$(-\frac{1}{2})$

* For each atom, the 2nd line coordinates, in parentheses, are those of the best-fit set.

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