# Determination of Atomic Parameters from Powder Diffraction Intensity Ratios

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The basis for a systematic use of intensity ratios is given in order to determine positional and occupational parameters. Given a series of $N$ powder diffraction intensities, the matrix of intensity ratios is defined. Expressing them as vectors, it is shown that they form a subset of $\frac{1}{2}$ $(N^2 - N)$ elements in a vectorial space with dimension $N - 1$. Since any intensity ratio may be obtained from the product or division of other ratios, their vectorial representation is used to define a criterion for independence for a set of ratios, transforming the product in a sum of the corresponding vectors. Any set of $N - 1$ independent ratios may be used in the determination of atomic parameters. In order to find the most suitable set, it is proposed to assign an index to each intensity ratio, which depends upon the difference between observed and calculated values and their derivatives with respect to the parameters to be determined. Then, an independent set of intensity ratios is chosen among those with higher indices, for each point of a convenient grid in the space of the parameters, finding the best set at each point. Finally, the best absolute set is defined as that with the minimum value of an agreement indicator between observed and calculated values. An illustrative example of the procedure indicated above is shown, and the results are compared with those obtained by other powder integrated intensity methods. In this work, comparison with the Rietveld profile refinement method is not considered.

## Introduction

Intensity ratios have often been used instead of original intensities in the determination of positional and occupational parameters from powder diffraction data (*1–3*). Using intensity ratios has the advantage that they are not so affected as the original intensities by factors which depend upon θ, especially when reflections at similar angles are selected. The error arising from preferential orientation of crystallites can also be diminished by choosing planes with similar orientation in the sample. In addition, intensity ratios can be chosen that are more sensitive to the variation of the parameters than the original intensities.

The selection of suitable ratios is usually performed by qualitative methods, and unpreferable ratios are often used. The result is possibly an unsatisfactory use of the method and perhaps the reduction of the number of parameters that reasonably can be determined.

The present procedure permits optimized selection of a set of intensity ratios by searching for pairs of reflections with similar relative errors.

## Theory

Given a series of observed or calculated powder diffraction intensities,

$$I(\vec{h}_1), I(\vec{h}_2), \ldots . I(\vec{h}_N),$$

or simply

$$I_1, I_2, \ldots I_N,$$

the $[I]$ $N \times N$ matrix defined by $I_{ij} = I_i/I_j$ is obtained.

It is clear that

1. $I_{ij} = (I_{ji})^{-1}$,

2. $I_{ii} = 1$.

Only the ratios $I_{ij} \geq 1$ with $i \neq j$ should be used in the determination of parameters, since their inverse ratios have nonequivalent contribution to agreement indicators. The total number of permitted ratios becomes $\frac{1}{2}(N^2 - N)$.

*Vectorial Representation of (i,j) Pairs*

One column of the matrix $[I]$ gives the values $I_1 I_2 \ldots I_N$ multiplied by $(I_j)^{-1}$. Similarly, a row is afforded by the inverse of the intensities multiplied by $I_i$. Any element $I_{ij}$, with $i \neq j$, can be obtained from the product or division of two elements of a row or a column. We say that a row or a column of the matrix $[I]$ forms a basis. We will take the first row, excluding $I_{11}$, as a basis:

$$I_{12} I_{13} \ldots I_{1N}.$$

The elements $I_{1i}$ may be expressed as

$$I_{1j} = (I_{12})^0 \times (I_{13})^0 \times \ldots$$
$$(I_{1j})^1 \times \ldots \times (I_{1N})^0,$$

permitting a correspondence between $I_{1j}$ and the exponents

$$I_{12} \rightarrow (1, 0, 0^{N-1}\ 0)$$
$$I_{13} \rightarrow (0, 1, 0^{N-1}\ 0)$$
$$\cdot$$
$$\cdot \qquad\qquad\qquad\qquad (1)$$
$$\cdot$$
$$I_{1N} \rightarrow (0, 0, 0^{N-1}\ 1).$$

The exponents may be considered as the components of a vector in a space with dimension $N - 1$, in which the vectors (1) form a base.

Any element $I_{ij}$, $i \neq j$, may also be expressed as

$$I_{ij} = (I_{12})^0 \times (I_{13})^0 \times \ldots \times (I_{1i})^{-1} \times \ldots$$
$$\times ((I_{1j})^1 \times \ldots \times (I_{1N})^0$$

or, in vectorial correspondence,

$$I_{ij} \rightarrow (0, 0, \ldots -1_{(i-1)} \ldots 1_{(j-1)} \ldots 0).$$

The set of vectors representing the pairs $(ij)$, $i \neq j$, forms a subset of vectors in a vectorial space with dimension $N - 1$, but they do not form a vectorial subspace. The product or division of two elements belonging to row 1 is associated with the sum of the corresponding vectors. In general the product or division of two or more elements of the matrix $[I]$ is associated to the sum of their vectors.

We are interested in the possibility of deriving intensity ratios by either the product of ratios or by the product of their inverses, which means that the elements $I_{ij}$ are identified with $I_{ji}$. Vectors representing $I_{ij}$ and $I_{ji}$ are opposite and may be identified by substituting the components 0, 1, or $-1$ by their class modulo 2; by doing so, $I_{ij}$ and $I_{ji}$ are represented by the same vector, the components of which take only the values 0 or 1. The sum and multiplication tables for mod. (2) classes are then to be used. The $\frac{1}{2}(N^2 - N)$ available elements of the matrix are represented as vectors with one or two nonzero components.

These vectors form a set $A$ of the vectorial space with dimension $(N - 1)$, defined on the two classes 0 and 1. In practice, they will be referenced indiscriminately as vectors or intensity ratios. The identification of $I_{ij}$ with $I_{ji}$ in the vectorial mapping holds whenever the independence of ratios is investigated; this will be discussed later. The agreement indicator is calculated only with ratios greater than unity, as stated above.

*Independence of (i,j) Pairs*

A subset of $A$ is linearly independent if

and only if their vectors are linearly independent. Speaking in terms of intensity ratios, independence is defined as the impossibility for a given ratio belonging to the subset to be obtained by the product or division of two or more intensity ratios belonging to the same subset. The maximum number of independent ratios (or vectors) is then $N - 1$.

The independence of a set of $N - 1$ vectors can be investigated, as in ordinary algebra, from the determinant of the $(N - 1) \times (N - 1)$ matrix composed of the $N - 1$ components of the $N - 1$ vectors, bearing in mind that the tables for the sum and multiplication of classes modulo 2 must be used. For a set of $N - 1$ linearly independent vectors, the value of the determinant is 1.

There is a simple algorithm for the calculation of the determinant. At least one row of the matrix has only one nonzero component, otherwise the determinant is zero. Let $I_{ij}$ be the unique nonzero component of row $i$. The expansion of the determinant $I_{ij}$ in terms of the elements of row $i$ and their cofactors is reduced to a single term, the value of which is the determinant of the $(N - 2) \times (N - 2)$ matrix obtained by deleting row $i$ and column $j$. If the process is repeated $N - 2$ times, the value of the determinant is obtained.

*Finding the Best Set of Independent Ratios*

The intensities are a function of the parameters to be determined, $I^c = f(u_1, u_2 \ldots u_n)$. For each point $\vec{u}$ in the $(u_1, u_2 \ldots u_n)$ space, intensities $I_1^c(\vec{u})\ I_2^c(\vec{u}) \ldots I_N^c(\vec{u})$ and the elements of a matrix $[I^c]$, $I_{ij}^c$ are calculated. The matrix $[I^c]$ has the same properties as $[I]$, and differs from $[I^o]$ in that $[I^c]$ is a function of the point $\vec{u}$ considered.

A new matrix $[\Delta]$ may be defined as $\Delta_{ij} = I_{ij}^o - I_{ij}^c$; this matrix allows us, simply by inspection, to find the values $(i,j)$, which

give the best agreement between observed and calculated values at each point.

However, in order to determine the parameters accurately, it has to be taken into account that different ratios are influenced in a different manner by the variation of the parameters, that is, the partial derivatives $\partial I_{ij}^c / \partial u_k$ take very different values. An index of merit $M_{ij}$, which allows for both factors $\Delta_{ij}$ and $\partial I_{ij}^c / \partial u_k$, is then defined for each $(i,j)$ pair. The index used is

$$M_{ij} = |\Delta_{ij}^{-1}| \cdot 1/n \sum_{k=1}^{n} \left| \frac{\partial I_{ij}^c}{\partial u_k} \right|,$$

although other indices may be investigated.

The term $|\partial I_{ij}^c / \partial u_k|$ is high when the intensities $i$ and $j$ vary in an opposite manner with $u_k$. The diffraction angles $\theta$ of intensities $i$ and $j$ may be similar or not. In the first case, $I_{ij}$ is almost independent of the average thermal factor $B$. The term $|\Delta_{ij}^{-1}|$ lowers the index $M_{ij}$ when the difference between observed and calculated ratios is high (i.e., due to preferential orientation of planes in the sample).

The $\frac{1}{2}(N^2 - N)$ different $(i,j)$ pairs are ordered in a list by their decreasing values of $M_{ij}$, and the best set at each point is defined as the set $B(\vec{u})$ formed by the first $N' \le N - 1$ independent ratios. With these, an agreement indicator between observed and calculated values may be obtained. Following Gastaldi *et al.* (*3*) the standard deviations of $\Delta_{ij}(\vec{u})$ were calculated:

$$\sigma_{B(\vec{u})} = \left[ 1/N' \sum_{N'} (\Delta_{ij}(\vec{u}) \right.$$
$$\left. - \langle \Delta_{ij}(\vec{u}) \rangle)^2 \right]^{1/2}, \qquad (i,j) \in B(u).$$

A map of $\sigma$ is obtained on a grid of discrete points. The set which gives the absolute minimum of $\sigma$ is the "best absolute set," and with this set, a new map of $\sigma_B$ may be obtained which permits a better determination of the parameters.

## Experimental and Results

The procedure described above was applied to the determination of positional parameters of oxygen in a natural almandine garnet. The contribution of oxygen to most structure factors in this garnet is small, making the power methods for the determination of their atomic parameters less accurate.

A gem-quality crystal was crushed and a powder sample was prepared with controlled crystallite sizes below 50 μm. The intensities were measured in an automated powder diffractometer, Philips APD-10. Intensities higher than $0.05 \ I_{max}$ were included, except for 420, 640, 800, and 664 reflections which have very small contributions of oxygen. A small fragment $0.2 \times 0.2 \times 0.3$ mm was separated from the same crystal to carry out a conventional refinement of atomic parameters (4) in order to compare the final results (Table I). The scattering factors were taken from (5).

X-Ray microprobe analyses were performed at several points of the crystal and average values were used. All experimental data are given in Table II.

To find the best set of intensity ratios at each point of a grid in a convenient region of the cell, a program was written for an HP-9845T computer. The program calcu-

### TABLE II

### EXPERIMENTAL DATA

Chemical analysis (wt%)

| Oxides: | SiO₂ | Al₂O₃ | FeO | MgO | CaO | MnO | |
|---|---|---|---|---|---|---|---|
| | 35.26 | 23.68 | 34.60 | 1.28 | 2.91 | 3.04 | Total: 100.76 |

Measured powder intensities

| N | hkl | $I_o$ | Estimated error (%) |
|---|---|---|---|
| 1 | 400 | 2685 | 2.4 |
| 2 | 332 | 623 | 8.19 |
| 3 | 422 | 2166 | 2.77 |
| 4 | 431 | 1663 | 3.18 |
| 5 | 521 | 2894 | 2.24 |
| 6 | 440 | 686 | 6.41 |
| 7 | 532 + 611 | 3721 | 1.94 |
| 8 | 444 | 3381 | 1.96 |
| 9 | 633 + 552 + 721 | 563 | 8.57 |
| 10 | 642 | 8790 | 1.25 |
| 11 | 811 + 741 | 291 | 15.18 |
| 12 | 840 | 2932 | 2.53 |
| 13 | 842 | 5319 | 1.71 |
| 14 | 754 + 930 + 851 | 419 | 10.76 |
| 15 | 862 + 10 2 0 | 780 | 6.00 |
| 16 | 864 + 10 4 0 | 3979 | 2.05 |
| 17 | 10 4 2 | 2080 | 3.19 |
| 18 | 884 + 12 0 0 | 1243 | 4.63 |
| 19 | 12 2 0 | 1637 | 3.66 |
| 20 | 12 2 2 + 10 6 4 | 2824 | 2.78 |

*Note.* Experimental conditions: Cu*K* radiation, graphite monochromator, 20 mA, 40 kV, scan step size 0.05°, time/step 2 sec, time/background, 10 sec.

### TABLE I

POSITIONAL, OCCUPATIONAL, AND THERMAL ($\times 10^4$) PARAMETERS FROM SINGLE-CRYSTAL DATA (STANDARD DEVIATIONS IN PARENTHESES)

| Wyckoff position | Atom | x | y | z | $f^a$ | U | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{23}$ | $U_{13}$ | $U_{12}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 48(h) | O | −0.0336(6) | 0.0487(6) | 0.1530(6) | | | 29(25) | 75(26) | 26(23) | 6(19) | 2(17) | −27(18) |
| 24(c) | Fe | 0.125 | 0 | 0.250 | 0.78 | | 5(37) | 43(40) | 43(40) | 16(11) | 0 | 0 |
| | Mg | | | | 0.05 | 77(96) | | | | | | |
| | Mn | | | | 0.07 | 77(96) | | | | | | |
| | Ca | | | | 0.08 | 77(96) | | | | | | |
| 24(d) | Si | 0.375 | 0 | 0.250 | 0.95 | | 84(25) | 96(22) | 96(22) | 0 | 0 | 0 |
| | Alᵗ | | | | 0.05 | 77(96) | | | | | | |
| 16(a) | Alᵒ | 0 | 0 | 0 | 1.00 | | 30(13) | 30(13) | 30(13) | 1(11) | 1(11) | 1(11) |

$R = 0.0733$
Number of reflections included: 161
Unit cell parameter: 11.545(4)

*a* Parameter not refined.

## TABLE III

### FINAL CRYSTAL DATA

| Method | Agreement indicator | $x$ | $y$ | $z$ | $B$ | Data |
|---|---|---|---|---|---|---|
| Single crystal | $R = 0.073$ | $-0.0336$ | 0.0487 | 0.1530 | | 161 structure factors |
| Intensity ratio | $\sigma = 0.096$ | $-0.0272$ | 0.0570 | 0.1524 | 3.34 | 17 ratios[a] |
| $R_I$ factor | $R_I = 0.117$ | $-0.0287$ | 0.0582 | 0.1506 | 3.31 | 20 powder intensities |
| Linear correlation coefficient | $r = -0.95$ | $-0.0326$ | 0.0617 | 0.1519 | 3.32 | 20 powder intensities |

| | Differences between results | | | |
|---|---|---|---|---|
| | $\Delta x$ | $\Delta y$ | $\Delta z$ | Distance (Å) |
| $R - \sigma$ | $-0.0064$ | $-0.0083$ | 0.0006 | 0.1212 |
| $R - R_I$ | $-0.0049$ | $-0.0095$ | 0.0024 | 0.1265 |
| $R - r$ | $-0.0010$ | $-0.0130$ | 0.0011 | 0.1511 |
| $\sigma - R_I$ | 0.0015 | $-0.0012$ | 0.0018 | 0.0304 |
| $\sigma - r$ | 0.0054 | $-0.0047$ | 0.0005 | 0.0829 |
| $R_I - r$ | 0.0039 | $-0.0035$ | $-0.0013$ | 0.0623 |

Unit cell parameter $a$: 11.545 Å
Space Group $Ia3d$

[a] Ratios used in decreasing order of $M_{ij}$: (2,18) (10,3) (5,4) (8,6) (7,18) (15,11) (13,16) (3,14) (7,17) (3,20) (8,14) (6,15) (17,14) (1,16) (1,3) (4,19) (19,18).

lates the scale factor $K$ and the average thermal factor $B$ from the well-known linear relation $\ln(I_o/I_c) = \ln K - 2B \sin^2\theta/\lambda^2$, where $\theta$ is the diffraction angle and $\lambda$ the wavelength used. Calculated diffraction intensities are obtained by the expression $I_c = K \exp(-2B \sin^2\theta/\lambda^2)|F|^2 pmA(\theta)$, where $F$ is the structure factor of the reflection, $p$ is the polarization factor, $m$ the multiplicity of the reflecting plane, and $A(\theta)$ the automatic divergence slit factor.

In the program only the 50 best pairs $(i,j)$ according to their index of merit $M_{ij}$ are used. Among these the first $N' \leq N - 1$ independent ratios are included in the calculation of $\sigma$.

The exploration of the region containing the $\sigma_{min}$ was performed in three stages. In the first stage, the distances between two consecutive points of the grid were $\Delta x = \Delta y$ $= \Delta z = 0.015$, permitting a rough localization of the minimum of $\sigma$. In successive stages the explored region was reduced, and the step between the two points was shortened, gaining precision.

The minimum value of $\sigma$, coordinates corresponding to it, and the best absolute set of ratios are given in Table III. The coordinates obtained by the $R_I$ factor (6) and Furuhashi et al. (7) methods, as well as those from single-crystal diffraction data, are also given.

Figures 1, 2, and 3 show the plots of the 17 $\Delta_{ij}$ functions against $x$, $y$, and $z$ parameters. $\Delta_{ij}$ curves intersect the straight line $\Delta = 0$ in segments centered on the values which give the $\sigma_{min}$. The errors of the parameters may be roughly estimated from these plots by the lengths of the intersection segments and are $E(y) > E(x) > E(z)$.
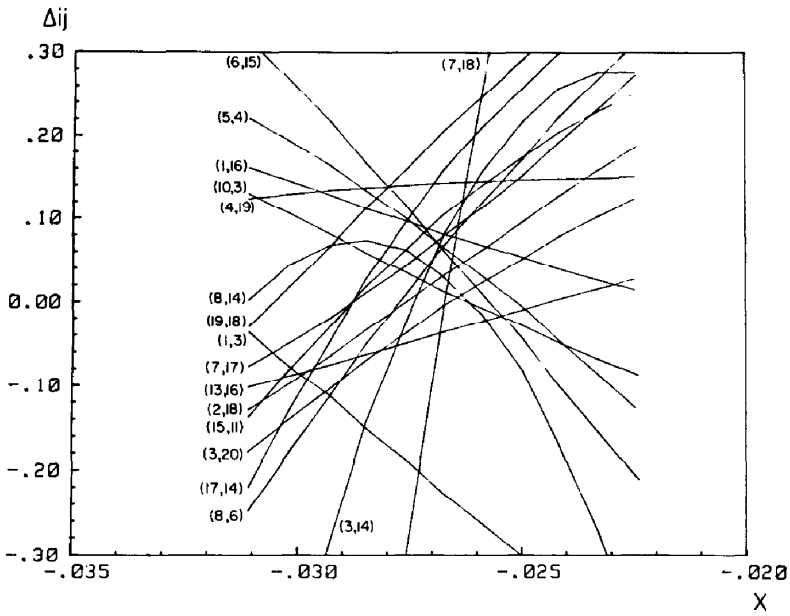
FIG. 1. Representation of $\Delta_{ij}$ curves as a function of $x$ parameter.
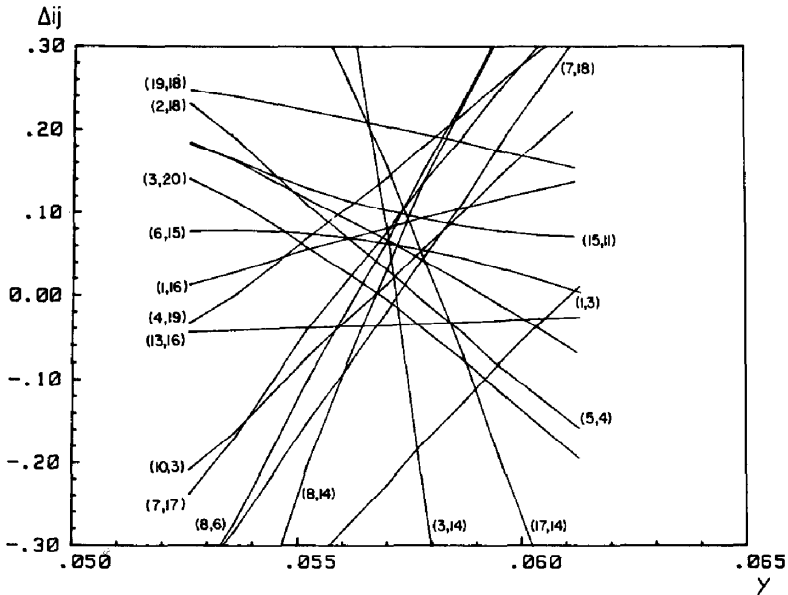
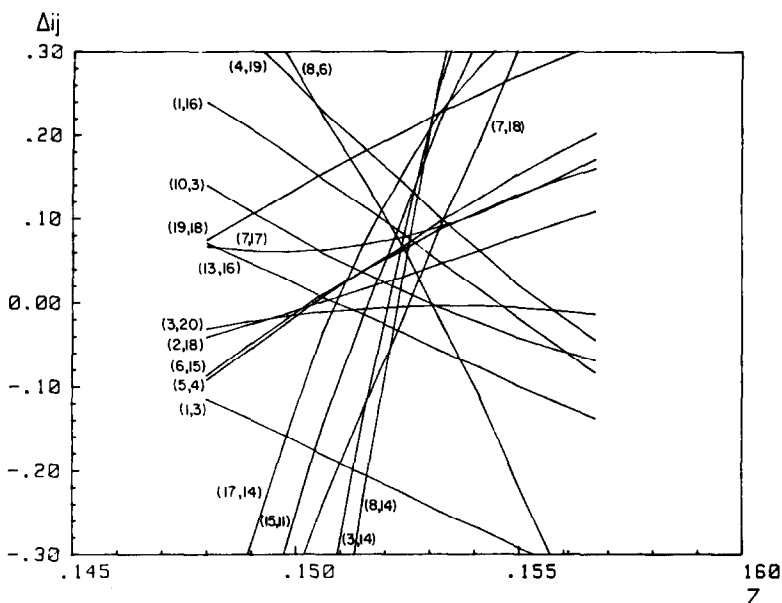FIG. 2. Representation of $\Delta_{ij}$ curves as a function of $y$ parameter.

FIG. 3. Representation of $\Delta_{ij}$ curves as a function of $z$ parameter.

## Discussion

In the discussion below, the results obtained from single-crystal data will be considered as an absolute reference for evaluating other results obtained from powder diffraction intensities.

The results given in Table III and Figs. 1, 2, and 3 show that using intensity ratios is a suitable method for the determination of positional parameters, even when they have low contributions to most structure factors. The main problem is to find a suitable set of such ratios, since different sets will lead in general to different results. The procedure indicated in the first part of this paper is considered a satisfactory one for finding the best set of ratios, defined as the "best absolute set."

In the present example of a garnet-type structure, the values obtained from ratios are only slightly better than those given by the $R_I$-factor method, probably due to the fact that the effect of preferential orientation of crystallites in the sample is negligi-

ble, but the effect of the overall isotropic temperature factor is by no means negligible in most intensity ratios used, and could be the main source of error in both methods.

The minimum zone localized on a $\sigma$-map is always very narrow, while the minimum for $R_I$ is wider. The localization of the parameters on the map of the linear correlation coefficient is less accurate, due to the broadness of the region of the maximum absolute value of $r$.

From the results given in Table III, it is seen that the parameters obtained by integrated intensity powder methods show a similar deviation from single-crystal values, namely, negative for $x$ and $y$ and positive for $z$. This fact suggests that the three methods present a common limitation with respect to the attainable accuracy, and that errors in such methods have to be estimated with circumspection. There are possibly inherent errors in all integrated intensity powder methods which may well arise from the difficulty of determining individual

isotropic temperature factors. The shifts between the values of $x$, $y$, and $z$ obtained from powder data and the corresponding values obtained from structure factors indicate these inherent errors in the present example.

## Acknowledgments

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