Bravais-Lattice Determination for Automatic Data Collection

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Abstract

A useful algorithm to find the Bravais lattice on a four-circle diffractometer is developed based on Delaunay's method of classifying the primitive cell. It consists of the evaluation of scalar products between lattice vectors and successive application of transformations to obtain the Bravais lattice. The procedures are found to be satisfactory in practical applications.

1. Introduction

The determination of a Bravais lattice from the reflection data is the first step in crystal-structure analysis. Though the development of the four-circle diffractometer has been very rapid, both in hardware and software, none of the programs is satisfactory enough to find the Bravais lattice automatically.

Delaunay (1933) presented the method of classifying the cells into 24 types and showed the relation to 14 Bravais lattices. Niggli (1928) published the basis for identifying the crystal system and lattice type from the scalar representation of the reduced cell. Buerger (1957) proposed methods of finding the reduced cell from an arbitrary primitive cell and Mighell & Rodgers (1980) proposed a method of determining lattice symmetry by considering metric symmetry.

However, for practical purposes of finding the Bravais lattice in crystal structure analysis, Delaunay's classification of crystal symmetry by pictorial diagram seems to be the most useful, because the algorithm of his method is easily coded on a small computer. We have developed software for finding the Delaunay cell and Bravais lattice without human intellectual aid; the performance of the system is shown to be satisfactory.

2. Delaunay cell

Delaunay's idea of classifying the primitive cell is illustrated by a tetrahedral diagram shown in Fig. 1. Three primitive translational vectors \( \mathbf{a}_0, \mathbf{b}_0, \mathbf{c}_0 \) and the inverted diagonal vector \( \mathbf{d}_0 = -(\mathbf{a}_0 + \mathbf{b}_0 + \mathbf{c}_0) \) are considered and the scalar products between them are

\[
\begin{align*}
P &= P_a \mathbf{P}_{T} + P_b \mathbf{P}_{R} + P_c \mathbf{P}_{S} + P_d \mathbf{P}_{U} \\
Q &= Q_a \mathbf{Q}_{T} + Q_b \mathbf{Q}_{R} + Q_c \mathbf{Q}_{S} + Q_d \mathbf{Q}_{U} \\
R &= R_a \mathbf{R}_{T} + R_b \mathbf{R}_{R} + R_c \mathbf{R}_{S} + R_d \mathbf{R}_{U} \\
S &= S_a \mathbf{S}_{T} + S_b \mathbf{S}_{R} + S_c \mathbf{S}_{S} + S_d \mathbf{S}_{U} \\
T &= T_a \mathbf{T}_{T} + T_b \mathbf{T}_{R} + T_c \mathbf{T}_{S} + T_d \mathbf{T}_{U} \\
U &= U_a \mathbf{U}_{T} + U_b \mathbf{U}_{R} + U_c \mathbf{U}_{S} + U_d \mathbf{U}_{U}
\end{align*}
\]

Fig. 1. Delaunay tetrahedral diagram, \( P, Q, R, S, T \) and \( U \) are the scalar products between the primitive translational vectors \( \mathbf{a}_0, \mathbf{b}_0, \mathbf{c}_0 \) and \( \mathbf{d}_0 = -(\mathbf{a}_0 + \mathbf{b}_0 + \mathbf{c}_0) \).

\[
\begin{align*}
\begin{pmatrix} 1 & 1 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} & \rightarrow \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 1 & 0 & 1 \end{pmatrix} \rightarrow \begin{pmatrix} 0 & 1 & 0 \\ 0 & 1 & 0 \\ 0 & 1 & 1 \end{pmatrix} \\
\begin{pmatrix} 0 & 0 & 1 \\ 1 & 0 & 0 \\ 0 & 1 & 0 \end{pmatrix} & \rightarrow \begin{pmatrix} 1 & 0 & 0 \\ 1 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \rightarrow \begin{pmatrix} 0 & 0 & 1 \\ 1 & 1 & 0 \\ 0 & 1 & 0 \end{pmatrix} \\
\begin{pmatrix} 0 & 1 & 1 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix} & \rightarrow \begin{pmatrix} 0 & 1 & 1 \\ 1 & 1 & 0 \\ 0 & 1 & 0 \end{pmatrix} \rightarrow \begin{pmatrix} 0 & 1 & 1 \\ 1 & 1 & 0 \\ 0 & 1 & 0 \end{pmatrix}
\end{align*}
\]

Fig. 2. Lattice transformations: matrices and resultant diagrams.

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BRAVAIS-LATTICE DETERMINATION

70

ations are used to transform the translational vectors either to be mutually orthogonal or to make obtuse angles. Actually, only a few operations are needed to complete this process and the six scalar products become all negative or zero. Then, we have translational vectors of the primary Delaunay cell, \( \mathbf{a}_p, \mathbf{b}_p \) and \( \mathbf{c}_p \).

Now we have the vectors that can be used to derive the basic Delaunay cell by equivalent transformations. These operations are shown in Fig. 3 by matrices: \( \mathbf{r}_a \) transforms \( \mathbf{c}_p \rightarrow \mathbf{a}_p, \mathbf{a}_p \rightarrow \mathbf{b}_p \) and \( \mathbf{b}_p \rightarrow \mathbf{c}_p \); \( \mathbf{M}_a \) changes \( \mathbf{a}_p \rightarrow \mathbf{a}_p, \mathbf{b}_p \rightarrow \mathbf{c}_p \) and \( \mathbf{c}_p \rightarrow \mathbf{b}_p \); and \( \mathbf{D}_a \) changes \( \mathbf{d}_p \rightarrow \mathbf{a}_p, \mathbf{b}_p \rightarrow \mathbf{c}_p \) and \( \mathbf{c}_p \rightarrow \mathbf{b}_p \). There is no operation that interchanges the partner relations \( P-S, Q-T \), and \( R-U \) without affecting other products in these transformations. However, if one of the scalar products has zero value, for example \( Q = 0 \), the operation \( \mathbf{Q}_a \) merely interchanges \( P \) and \( U \). By this type of procedure the quadruple vectors are modified. Applying these transformations at least several times, we have the basic Delaunay cell vectors, \( \mathbf{a}_d, \mathbf{b}_d \) and \( \mathbf{c}_d \).

3. Classification of 24 Delaunay cells

The practical procedure begins with the numbering of \( P, Q, R, S, T \), and \( U \) in the order of their absolute value. When one of them is zero, it is labelled \( 0 \) and, if there is more than one zero value, the labelling is repeated. Equal value of the scalar product is counted by the same number starting from \( 1 \). With this rule, the largest labelling number is equal to the number of the kinds of non-zero values.

The number of occurrences of zero is denoted by \( N_z \) and the number of occurrences of equal value in the scalar products by \( N_s \). \( N_z \) and \( N_s \) are used to classify the cell.

The next step is to compare the values of \( P \) and \( S \), and put the smaller one to the outer edge in Fig. 1 by the transformation \( \mathbf{D}_b \) or \( \mathbf{D}_c \). Similar replacement is made for the pairs \( Q-T \) and \( R-U \). This does not always proceed consistently; in this case the sum of three scalar products on the inner edges is maximized.

Now let us classify the Delaunay cell according to the number \( N_z \).

(1) \( N_z = 3 \). In this class, three translational vectors \( \mathbf{a}_d, \mathbf{b}_d \) and \( \mathbf{c}_d \) are orthogonal to each other. There are three cases as shown in Fig. 4. In the case for \( N_z = 2 \), we may use the operation \( \mathbf{r}_a \) or \( \mathbf{r}_b \) to put \( U \) in the position as shown in the middle of Fig. 4. If \( N_z = 1 \) the size of the lattice is given by \( a = (-S)^{-1/2}, \quad b = (-T)^{-1/2}, \quad \) and \( c = (-U)^{-1/2} \). The ordering of \( c < a < b \) and the choice of right- or left-handed coordinates are not taken into account at this stage.

(2) \( N_z = 2 \). There are two types, I and II, with regard to the position of zero, as shown in Figs. 5 and 6.

*In actual experiment, the judgement whether the product is zero or whether two of them are equal is made considering errors inherent to each measurement. A criterion for maximum error \( \Gamma \) as \( \Gamma = (\text{cell volume})^2 \cos(\theta) \) (\( \theta \) is \( 0.1 \sim 0.2^\circ \)) was used.

Fig. 4. Basic Delaunay cells for \( N_z = 3 \) and transformation matrices to obtain the conventional Bravais lattices.

Fig. 5. Basic Delaunay cells for \( N_z = 2 \) (type I) and transformation matrices to obtain the conventional Bravais lattices.

Fig. 6. Basic Delaunay cells for \( N_z = 2 \) (type II) and transformation matrices to obtain the conventional Bravais lattices.
respectively. Scalar products with zero value do not appear in the partner relation in type I, while they are in type II.

Type I. If the hexagonal lattice has \( c = 2^{1/2}a \), then \( U = S \) accidentally and \( N_s \) happens to be 4, but this is a special case of \( N_s = 3 \). \( U \) in Fig. 5 is the unique position not transformed into the other position by equivalent transformations. In the case of \( N_s = 3 \), if \( U \) takes another position in Fig. 5, the tetrahedral diagram can be changed into a special case of \( N_s = 2 \) (apparently it is \( N_s = 3 \)) by equivalent transformation. In the case of \( N_s = 2 \), if \( U \) and \( S \) are interchanged, a similar situation occurs, then it is regarded as a special case of \( N_s = 1 \).

The value of \( R \) in \( N_s = 1 \) (monoclinic cell) is chosen so as to be the smallest absolute value among \( R \), \( S \) and \( T \) by using the operation \( P_a \) or \( Q_b \), because \( ac \cos \beta \) is chosen to be smallest in ordinary convention.

Type II. In this type all positions except zero can be changed. In the case of \( N_s = 2 \), the value of \( Q \) is chosen

![Fig. 7. Basic Delaunay cells for \( N_s = 1 \) and transformation matrices to obtain the conventional Bravais lattices.](image)

![Fig. 8. Basic Delaunay cells for \( N_s = 0 \) and transformation matrices to obtain the conventional Bravais lattices.](image)

4. Practical applications

We have developed an algorithm to find the Bravais lattice using a four-circle diffractometer. The program system consists of: (1) peak search scanning around the four axes yielding reciprocal vectors. (2) The vector minimum method applied for finding the shortest reciprocal-lattice vectors that lead to the primitive-lattice vectors. (3) The Delaunay method used to find the Bravais lattice by the algorithm shown above. (4) Intensity measurement of the equivalent reflections in order to confirm the Laue symmetry of the estimated Bravais lattice. The correlation coefficients between pairs of observed reflections are statistically evaluated. If the coefficient is sufficiently large, we establish the Bravais lattice and the Laue group and proceed to automatic data collection.

The algorithm was tested first on the data provided by computer simulation of cubic, hexagonal, tetragonal, orthorhombic, monoclinic and triclinic crystal systems. Real crystals of known structures were then examined on a diffractometer (Rigaku AFC-5R) combined with a mini-computer (PANAFACOM U-1200), and the performance of the combined system was shown to be satisfactory. Then we used the whole system for the crystal structure analysis through the automatic data collection program and about sixty crystal structures have been solved without any trouble. The symmetries of these crystals belong to
P2₁/c, P1̅, C2/c, C2/m, Pbcn, P2₁ or P1. Although our experience is limited, we have not found any confusion about crystal symmetry.

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