Converse-transformation analysis

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(Received 19 August 1991; accepted 29 August 1991)

Abstract. Converse-transformation theory and NIST*-LATTICE open a new approach to study many theoretical and practical problems in crystallography. In this approach a new operator, the converse-transformation operator, is defined. The focus of this approach is based on the calculation of groups of matrices relating two lattices and subsequent analysis of these matrices to deduce crystallographic relationships. An efficient algorithm has been designed that has the ability to find all matrices (H) that relate ANY two cells (no matter how skewed) to within any specified tolerances (t) of the cell parameters. A Fortran program, NIST-LATTICE, that enables this new approach to be used is available to the scientific community. There are many immediate applications of converse-transformation analysis including the full automation of the single-crystal diffractometer and phase characterization using lattice-matching techniques.

Introduction. Converse-transformation theory and NIST*-LATTICE (Karen & Mighell, 1991) permit a new approach to many theoretical and practical problems in crystallography. The objective of this new approach is to determine groups of matrices relating ANY two lattices and to use these matrices in the subsequent analyses which focus on the nature of the matrices. Many types of inter- and intralattice relationships can now be subjected to powerful mathematical analyses.

This approach has applications in many areas of crystallography. For example, it can be used in symmetry determination (Himes & Mighell, 1987), in protein crystallography (Mighell, Rodgers & Karen, 1991), in phase characterization using the analytical electron microscope (Mighell & Himes, 1990), in establishing compound relationships within and between databases containing crystalline materials, in the study and prediction of epitaxic growth and in all areas in which the crystalline lattice plays a role.

Discussion. We define a new operator, the converse-transformation operator, as follows:

\[ \text{CT}_{h,t}(Y,Z) = \left\{ (H,T)_{i,j} \right\} \]

where \( h, t \) represent the domains of \( H, T \), respectively, and \( Y, Z, H, T \) represent vector triples in \( R^3 \) (Karen & Mighell, 1989).
these two applications, Y and Z are two cells. H represents a transformation matrix relating Y and Z and T is the corresponding tolerance matrix.

(1) Relate two lattices (REL). In this application of the CT operator, the REL program function in NIST-LATTICE allows the user to relate ANY two cells using the specified matrix elements, \( h \), and input tolerances, t. Specifically, all transformation matrices, \( H \), relating input \( \text{CELL} \, 2 \) to \( \text{CELL} \, 1 \) are generated. The output tolerance matrix, associated with a matrix \( H \), represents how closely the transformed \( \text{CELL} \, 2 \) agrees with \( \text{CELL} \, 1 \) and is of the form

\[
\begin{align*}
tol_a & \quad tol_b & \quad tol_c \\
tol\,\alpha & \quad tol\,\beta & \quad tol\,\gamma.
\end{align*}
\]

Thus, if \( \text{CELL} \, 2 \) is defined by \( A2, B2, C2, \text{ALPHA}2, \text{BETA}2, \text{GAMMA}2 \), then the transformation of \( \text{CELL} \, 2 \) by matrix \( H \) will give a transformed cell having lattice parameters \( A1 + tol\,a, ..., \text{GAMMA}1 + tol\,\gamma \). Using this program function, one can readily determine the nature of the relationship between two cells including sub/supercell and composite relationships.

(2) Symmetry determination (SYM). In sharp contrast to other methods which focus on the consequences of symmetry (such as dot products, \( d \) spacings etc.), this approach deals with symmetry in its most abstract form – represented as matrices. The basis of the SYM program function is to generate a group of matrices reflecting the holohedry of the lattice. This is accomplished through a specialized application of the converse-transformation operator, defined above.

The SYM program function generates the matrices, \( H \), that relate ANY primitive cell of the lattice to itself. In theory, it is the nature of the matrices themselves that defines the set to be analyzed (i.e. those defining a symmetry group). In practice, however, the usual result is that the tolerance matrices alone clearly define the groups and all that is required to determine metric lattice symmetry and pseudosymmetry is to count. The numbers of matrices for the seven lattice metric symmetries are: triclinic, 1; monoclinic, 2; orthorhombic, 4; rhombohedral, 6; tetragonal, 8; hexagonal, 12; and cubic, 24.

Generated with each symmetry matrix is a tolerance matrix of the form

\[
\begin{align*}
tol\,a & \quad tol\,b & \quad tol\,c \\
tol\,\alpha & \quad tol\,\beta & \quad tol\,\gamma.
\end{align*}
\]

Simply by averaging the group of tolerance matrices, an error matrix is calculated that may be compared directly to the e.s.d.'s for the primitive cell. More importantly, this error matrix (= averaged tolerance matrix) may be used to calculate an idealized cell reflecting exact metric symmetry (i.e. idealized cell = \( A1 + av\,tol\,a, ..., \text{GAMMA}1 + av\,tol\,\gamma \)). By incorporating information from both sets of matrices, \( H \) and \( T \), the idealized cell provides a unique means of evaluating experimental error based on ALL the symmetry operations of the lattice. This is crucial when determining standard or conventional cells.

When evaluating symmetry using CT analysis, the experimentalist need not rely solely on metric information. The group of \( H \) matrices may be viewed as sets of equivalent \((h,k,l)\)'s represented in matrix form. Write the indices of a known reflection as a column matrix and premultiply by \( H \) to generate sets of reflections that should have equivalent intensities if the metric and crystal symmetries agree.

Once the symmetry and error have been evaluated, obtaining a transformation matrix to a standard or conventional cell may be accomplished either through analysis of the \( H \) matrices themselves or by inputting the idealized cell reflecting the exact metric symmetry into a reduction program function in NIST-LATTICE with subsequent table look-up. (Note that this is possible ONLY after the symmetry and experimental error have been evaluated through CT analysis.)

For additional details as well as discussions of other theoretical and practical applications in crystallography, see Himes & Mighell (1987).

Conclusion. In conclusion, the CT theory and NIST-LATTICE provide a theoretical and practical basis for a fundamentally new approach to crystallography and should routinely be used. The ability to find efficiently ALL matrices \((H)\) that relate ANY two cells (no matter how skewed) to within a given specified tolerances \((t)\) of the cell parameters permits one to establish many important inter- and intralattice relationships. The implications of this in crystallography as well as in mathematics are many. Many existing procedures will improve and new types of analyses are possible.

In diffractometry, this new approach provides, for the first time, the required theory to automate reliably a single-crystal diffractometer so that all critical steps can be carried out in a logical order and that no risky assumptions are necessary. This application alone will dramatically improve diffractometry and will prevent errors in symmetry of the type that are currently being published at a much too frequent rate. In identification, this approach provides the basis to identify uniquely an unknown against a large database (e.g. NIST CRYSTAL DATA) using lattice-matching techniques. In data evaluation and in materials design, one can establish relationships among entries within and between databases containing crystalline materials.

In theoretical work, one can calculate and work with groups of symmetry matrices with respect to any reference system no matter how skewed.

Availability. The experimentalist can carry out CT analysis via the NIST-LATTICE program. This program is written in standard Fortran and is designed to be used in any analytical laboratory. The software is multifunctional and
can be used to analyze various types of lattice relationships. The present version of the program performs several functions including: (1) the determination of symmetry and the evaluation of experimental error through converse-transformation analysis; (2) the generation of transformation matrices relating any two unit cells; (3) the calculation of the reduced cell of the lattice and the calculation and reduction of specified derivative supercells and/or subcells; (4) unit-cell transformations and matrix inversions. It is planned to incorporate additional features in forthcoming versions of this program. To obtain a copy of the program write Vicky Lynn Karen at the above address.

References