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SOFTWARE NOTICE

LCLSQ: Lattice parameter refinement using correction terms for systematic errors

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ABSTRACT

Version 8 of the least-squares lattice parameter refinement program LCLSQ is now available. This new version incorporates several improvements, the most important of which are the availability of correction terms for powder diffractometer systematic errors and a code for calculating values of d and 2θ with omission of systematic space-group absences following refinement.

INTRODUCTION

LCLSQ is a general least-squares lattice parameter refinement program that employs indexed powder or single-crystal diffraction data. It uses a method originally outlined by Cohen (1935) and described in detail by Burnham (1962) that expands Bragg's law to include systematic errors in θ. Up to nine different correction terms for systematic errors may be included in the least-squares refinement. The mathematical form of each term can be selected to represent any one of nine distinct kinds of systematic error. The correction terms determined by refinement correspond to experimental factors that relate either to the instrument or the sample; initial values of these terms may be provided, if known. Up to 200 measurements of 2θ or d (which may be weighted or not, as appropriate) with assigned indices hkl, from one or more diffraction records of the same substance, constitute the observations.

Values of d and 2θ for up to 1000 hkl's may be calculated using the refined lattice parameters. The 2θ range and up to three wavelengths are selected by the user. If the space group is known, systematic absences may be excluded from the generated list. Observed d values are matched with calculated ones.

REFINEMENT WITH SYSTEMATIC CORRECTION TERMS

The original Fortran version of LCLSQ was written in the mid-1960s. It could include correction terms for several systematic errors associated with either powder or Weissenberg single-crystal film methods: front- and back-reflection film shrinkage, specimen absorption, and camera eccentricity. Burnham (1965) demonstrated that judicious use of these correction terms improved the accuracy of refined lattice parameters and usually gave more realistic, but typically larger, estimated standard errors, compared with conventional refinements with no corrections for systematic errors. Refinements using mutually inconsistent data sets (for example, from separate films with different amounts of shrinkage, from different cameras with distinct instrumental errors, or from different powder mounts or single crystals of the same sample) generally led to the same refined lattice parameters (within errors) when appropriate systematic error correction terms were included. Separate refinements with these data sets using no systematic error correction terms invariably led to sets of lattice parameters that differed significantly, usually by many times the indicated least-squares errors.

Tests with LCLSQ Version 8 using powder diffractometer data with systematic error correction terms corroborates the earlier experiences. Burnham and Bish (in preparation) show that several data sets obtained with NBS standard Si, using a variety of metallic shims to alter specimen displacement (relative to the diffractometer focusing circle), yield nearly identical refined lattice parameters. These parameters are close to the NBS reported value, when correction terms for sample displacement, sample transparency, and axial divergence are included. The least-squares values for sample displacement match closely the measured shim thicknesses. A refinement using all the data sets simultaneously, with one correction term for axial divergence and one for sample transparency plus separate sample displacement correction terms for data from patterns obtained with different shims, yields a lattice parameter identical with the NBS standard value. Additional tests with a data set for corundum, on which an artificial zero two-theta error (an error in definition of the position for which $2\theta = 0°$) of $+0.04°$ was imposed, yield exactly that value for zero two-theta error plus values for axial divergence error, sample displacement error, and lattice parameters identical to those obtained with the unadulterated data set. Tests with Straumanis-type Debye-Scherrer film data (both front and back reflections) similarly extract the correct values of artificially imposed film shrinkage errors.

An important point to be made is that successful lattice parameter refinement with systematic error correction terms requires 2θ or d_{hkl} observations that are as free as possible of random measurement error.

FEATURES OF LCLSQ VERSION 8

There are several enhancements incorporated in Version 8 of LCLSQ that improve its performance relative to older versions.

Some aspects of the refinement process have been automated. Least-squares iterations are automatically made until convergence criteria have been met or a maximum number of cycles have been completed. Default values for either of these conditions can be overridden by the user. Only those lattice parameters whose values are independently variable for the stated lattice type (crystal system) need be provided as input; each of these will normally be varied. The user may, however, vary any subset of these lattice parameters as conditions warrant. For example, if only $hk0$ data are available for an orthorhombic sample, the user would manually select a and b to be varied, instead of letting the program automatically vary a, b, and c.

From zero to nine systematic error corrections terms may be refined. Each term is selected by the user to be one of nine types: errors in diffractometer data due to sample displacement, sample transparency, axial divergence, or zero two-theta error; or errors in film (Debye-Scherrer or single-crystal) data due to absorption

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(either the Taylor-Sinclair or Bradley-Jay approximation), front- or back-reflection film shrinkage (including camera radius errors), or camera eccentricity.

Refined correction terms are reported as physically interpretable numbers, e.g., sample displacement in millimeters toward (−) or away from (+) the center of the diffractometer focusing circle, axial divergence in degrees, film shrinkage errors as fractional change, and either + (expansion) or − (contraction). Terms that must be positive (axial divergence, sample transparency, and absorption) will be reset to or fixed at zero if they refine to negative values. If instrumental systematic error terms (e.g., axial divergence, zero two-theta error, camera eccentricity) are known from prior experience or calibration, their values may be provided and either refined or not, depending on circumstances. The functional dependence of each kind of systematic error on θ has been programmed following relationships given by Klug and Alexander (1974).

An ordered list of values of d and 2θ may be calculated following refinement. The 2θ range is set by the user. Up to three wavelengths, the same or different from those of the observed data, may be selected. If the space group is known, systematic absences can be excluded. Observed data are matched with calculated data. If matching takes place and $2\theta_{min}$ is 0°, the Smith-Snyder Figure of Merit is provided (Smith and Snyder, 1979). Calculation of values of d and 2θ may be performed alone, with no prior lattice parameter refinement; in this case, the input file need contain only lattice parameters and wavelengths with no observed data.

Input is provided in a separately prepared file that is specified to the program at the beginning of execution. Output is written to a file named and opened during execution. Execution times depend on machine configuration; refinement of all lattice parameters and several correction terms for a triclinic sample may take from a few seconds with 286- or 386-based machines to around one minute with an early IBM XT. A math coprocessor will improve performance by approximately 15–20%.

Requirements and availability

Version 8 of LCLSQ is written in Fortran for IBM PC/XT/AT and compatible computers, and will operate with or without a math coprocessor. It requires approximately 150K of available memory; no graphics are used. The program is available from the author on either two 5¼″ diskettes or one 3½″ diskette (normal density). The package includes two executable modules (one for use with a coprocessor, the other without), complete source code, input and output files for five sample problems, and an instruction manual. The cost is $20 to individuals at educational and other nonprofit institutions, or $100 to commercial organizations and their employees. For information about licensing arrangements, contact the author.

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