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. 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.

An important point to be made is that successful lattice parameter refinement with systematic error correction terms requires 2θ or d 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 has 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 hkl 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...
(either the Taylor-Sinclair or Bradley-Jay approximation), front-
or back-reflection film shrinkage (including camera radius er-
rors), or camera eccentricity.

Refined correction terms are reported as physically interpré-
table 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 frac-
tional 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., ax-
ial 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

An ordered list of values of d and 2θ may be calculated fol-
lowing 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 cal-
culated data. If matching takes place and 2θ_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 pa-
rameters 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 (nor-
mal 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 organi-
izations and their employees. For information about licensing
arrangements, contact the author.

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