Technical Information and Caveats

PASCal has been designed to be user friendly and as a result does not implement many of the more advanced forms of fitting possible. There are a number of other (offline) codes that can carry out these kinds of fits and we recommend using them if you require this more advanced functionality.

Errors

The errors calculated for both linear and non-linear fitting do not directly take into account the T/P errors provided (in effect they only act as weights). This usually provides a reasonable approximation as typically the inherent scatter of the strain is the primary source of error. In the case that the data has very small errors, this method will overestimate the magnitude of the errors. It can also prove inaccurate for small data sets.

It is possible if you have the magnitudes of the errors on your lattice parameters to propagate those errors through to get more accurate estimates and WINStrain can give you errors on strains from errors on lattice parameters. However, to get the most accurate estimate of errors it is also necessary to include the covariance of lattice parameters, as correlations are likely to be significant too and for low symmetry systems, the inclusion of errors in lattice parameter angles in strain errors is a problem with no unique solution. Unfortunately, the errors that are calculated from Rietveld fits or single crystal calculations often seem to underestimate the true errors in lattice parameters and so will underestimate the true error in your calculated values if used naively (see Haestier, *J Appl. Cryst* **2009**, *42*, 798, Herbstein, *Acta Cryst B* **2000**, *56*, 547; Taylor, R. & Kennard, O. *Acta Cryst B* **1986**, *42*, 112.)

In PASCal, linear fits use White's heteroscedascity consistent error estimates and non-linear fits use the residuals to calculate the error estimates.

Fitting

As PASCal does not use cell-parameter or volume errors in fitting or strain calculation, users may also wish to use another software program to carry out these kind of calculation if they wish to examine this data more finely. The contribution of volume errors to final errors is discussed in Angel (Reviews in Mineralogy and Geochemistry, Vol. 41, High-Temperature and High Pressure Crystal Chemistry **2000**)

The fits for non-linear equations of state can be unstable, especially if the equation of state does not describe the behaviour well. Even where this instability occurs, it does not often seem to perturb the fitted parameters too badly. The errors, being derived from the derivatives of the parameters, are much more susceptible to instabilities and failure to converge. As the input errors (as currently implemented) act simply as weights, multiplying the errors by a constant can tweak the fit and hopefully produce convergence.

The ambient pressure (or critical pressure) data points can have outsize effects on the fitted parameters for both the Birch Murnaghan and empirical equations of state. Care should be taken with this point.

As different equations of state are used for the principal axis and volume fits, they should not be expected to produce self-consistent results. If instead of volume, a cubed length is fitted, the Birch-Murnaghan equation of state can be used to fit a length, which should give consistency. These values are provided lower on the PASCal output page. The non-linear nature of the fitting means that these values are not guaranteed to be self-consisten either. Other equations of state are of course in use and may be more appropriate for some materials.

Strain Calculation

PASCal calculates infinitesimal Lagrangian strains by default. These may not be appropriate for large changes and is not formally consistent with the Birch-Murnaghan derivation. Options to use finite and/or Eulerian strains are provided. PASCal also uses a numerical approach that means the strains calculated

are effectively averages of both direction and magnitude. It assigns the strain to the axes by simple numerical ordering. This can cause problems if two axes swap in magnitude. Fitting of the calculated strains outside of PASCal is currently the best approach for these kinds of systems. The directions of the principal axes are taken, like the compressibilities, from the median data point.

Other programs:

WINstrain and EOSfit (**http://www.rossangel.com/**)

A pair of useful programs for Windows. WINStrain provides a large number of different options for calculating strains from lattice parameters. EOSfit is fitting program for equations of state.

STRAIN (**http://www.cryst.ehu.es/cryst/strain.html**)

Bilbao crystallographic server carries out strain calculations for a single pair of lattice parameters.

DEFORM (**http://www.ill.eu/instruments-support/computing-for-science/cs-software/all-software/deform/**)

Untested, however DEFORM has also been used in the literature for strain calculations.

If you know of any other useful software that should be added to the list or have any other questions, please email **matthew[dot]cliffe[at]chem[dot]ox[dot]ac[dot]uk**