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EosFit7-GUI: a new graphical user interface for equation of state calculations, analyses and teaching

Javier Gonzalez-Platas,^a Matteo Alvaro,^b Fabrizio Nestola^c and Ross Angel^{c*}

^aDepartamento de Física, Servicio de Difracción de Rayos X, Universidad de La Laguna, La Laguna, Tenerife E-38206, Spain, ^bDepartment of Earth and Environmental Sciences, University of Pavia, Via A. Ferrata 1, Pavia 27100, Italy, and ^cDepartment of Geosciences, University of Padova, Via G. Gradenigo 6, Padova 35131, Italy. *Correspondence e-mail: rossjohnangel@gmail.com

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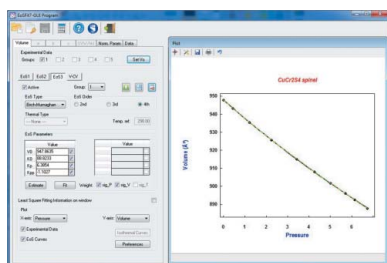
Keywords: equations of state; thermal expansion; high pressure; high temperature; low temperature; elasticity.

EosFit7-GUI is a full graphical user interface designed to simplify the analysis of thermal expansion and equations of state (EoSs). The software allows users to easily perform least-squares fitting of EoS parameters to diffraction data collected as a function of varying pressure, temperature or both. It has been especially designed to allow rapid graphical evaluation of both parametric data and the EoS fitted to the data, making it useful both for data analysis and for teaching.

1. Introduction

The primary details obtained when crystals are studied by diffraction measurements under non-ambient conditions (*i.e.* with changes in pressure and/or temperature) are the unit-cell parameters and the unit-cell volume. The relations between the volume, pressure and temperature are defined by the equation of state (EoS) of the material, and analogous equations exist for the unit-cell parameters. The parameters of these EoSs also define how the compressibility, thermal expansion and bulk elastic properties of the material change in response to compression and expansion. The normal procedure is to determine the EoS parameters, such as the bulk modulus, its pressure derivatives and their dependence on temperature, by fitting an EoS model to experimental P - V , V - T or P - V - T data (Angel, 2000). The same process can be applied to unit-cell data obtained from computer simulations. Some authors use spreadsheets for this process, or general fitting programs, in which the user has to define the equations for particular EoS models, thus introducing the possibility of generating errors in the calculations. Fortunately, there are many programs specializing in this type of calculation. One of them is the *EosFit7c* program (Angel *et al.*, 2014), which uses a library of validated subroutines to perform EoS fitting and calculations. However, *EosFit7c* is a command-line program without graphical facilities; graphs and results can only be plotted by exporting the EoS and data to external plotting programs.

We have now developed a version of *EosFit7* with a full graphical user interface (GUI), specifically designed as an interactive easy-to-use tool for data analysis and teaching. For both applications, an immediate graphical presentation of the results of a chosen analysis or fit is required, so *EosFit7-GUI* includes all of the types of plot required for a complete EoS analysis. It also includes facilities for fitting EoSs to the data, and utilities for performing all of the most common EoS calculations. Recently published examples using *EosFit7-GUI*



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include the determination of the high-pressure EoS of MgO_2 (Lobanov *et al.*, 2015), the high-temperature behaviour of zeolite ZSM-5 (Ardit *et al.*, 2015) and the high-pressure electronic behaviour of SnS_2 (Filsø *et al.*, 2016).

EosFit7-GUI is built on the same subroutine library as the *EosFit7c* program and therefore allows the use of any of the thermal-expansion equations and EoSs that are available in *EosFit7c*. We have specifically limited the features in the GUI so as to keep the interface simple and intuitive, so that the program can be easily learnt and easily used for teaching. Therefore, *EosFit7-GUI* does not include facilities for the direct fitting of elastic moduli (Milani *et al.*, 2016) or continuous structural phase transitions (Angel *et al.*, 2016), because these would require many additional controls to be added to the GUI. However, this is not a serious limitation because the *EosFit7-GUI* program uses exactly the same format as *EosFit7c* for all input and output files. Thus, data and results can be interchanged immediately between the two programs, allowing the GUI user to move data analysis easily to the *EosFit7c* program when its more advanced features are required, and subsequently use the GUI for plotting the results.

2. Program features

The main window of the program is divided into two major zones (Fig. 1). The left-hand zone is dedicated to a series of tabs (described in detail below) that allow the user to select data and define EoSs, to control the fit of EoS parameters to the data, and to select data and EoSs for plotting. The right-

hand zone is dedicated exclusively to a graphical display of the data and/or EoS parameters.

2.1. Experimental data

The program reads experimental data from a text file in the same format as used with the *EosFit7c* program (Angel *et al.*, 2014). These simple-format keyword-directed data files can be prepared with any text editor or by exporting them from spreadsheet software, and can contain all of the unit-cell parameters and, if available, their estimated standard deviations. Once loaded into the GUI, the data can be inspected in the data tab, which resembles a spreadsheet display. The philosophy of the *EosFit7* suite of programs is to avoid editing data files, as this inevitably leads to corruption of data. Therefore, the data tab includes the possibility to select or deselect individual data items, which allows them to be included in, or excluded from, EoS fitting and display. Data can be grouped, which allows blocks of several data items to be selected or deselected together. The selection of data by groups facilitates the handling of P - V - T data, for example by allowing the data collected within a narrow temperature range to be first fitted with an isothermal EoS prior to fitting the entire data set simultaneously with a single P - V - T EoS. It also allows for the fast and easy analysis of data sets that include discontinuous phase transitions.

2.2. Defining and fitting EoSs

EosFit7-GUI distinguishes between volume and linear EoSs. One tab is assigned to each of V , a , b and c in the left-hand zone of the GUI (Fig. 1), and there is an additional UVW/hkl tab that allows the user to select a plane-normal direction specified by the Miller indices (hkl) or a lattice direction specified by the zone-axis symbol [UVW]. This last tab allows a student to explore how, for example, compressibility varies with direction in any crystal system. In the analysis of monoclinic and triclinic materials, this tab allows the principal axes of compression or expansion, which may not lie along the chosen unit-cell axes, to be directly fitted with EoSs.

These five tabs provide identical facilities and are the core control area for data fitting, EoS manipulation and results display. The user can switch between them without losing any data or results. Each tab contains the possibility to define up to three different EoS models that can be displayed simultaneously for ease of comparison (Fig. 2). The user can define each EoS independently, by selecting the EoS type from the pull-down menus, selecting the order of the EoSs and

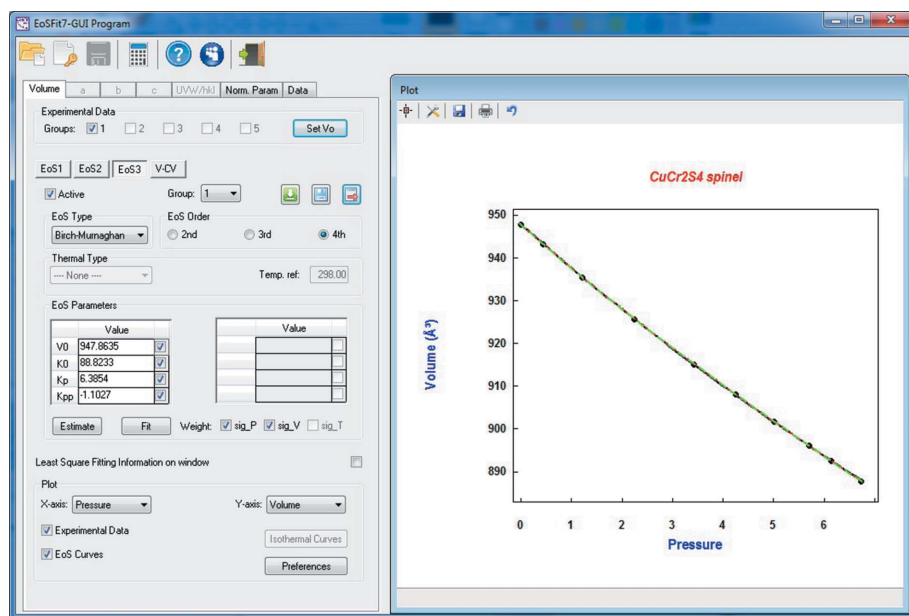


Figure 1

The main window of the *EosFit7-GUI* program, showing the control tabs in the left-hand zone and the graphics zone for plotting. The compression data are a thiospinel, CuCr_2S_4 (Alvaro *et al.*, 2014), with the fits of second- (black), third- (red) and fourth-order (green) Birch–Murnaghan EoS shown as lines. The same data and fits are also shown as f - F plots in Fig. 4.

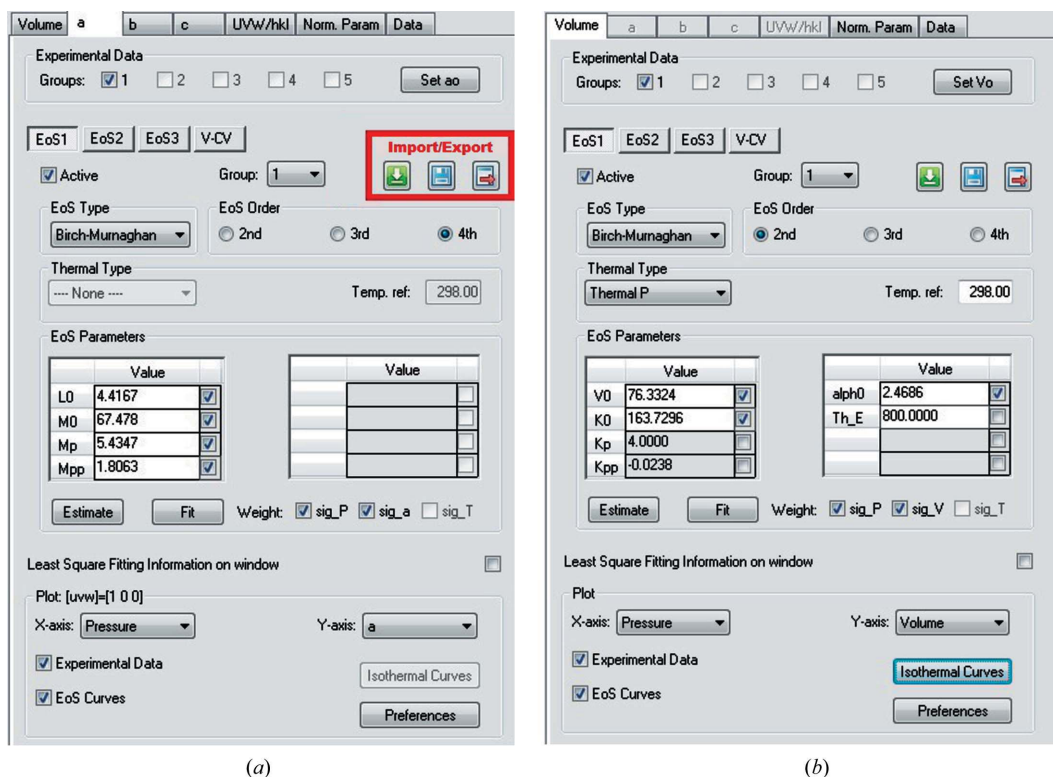


Figure 2

Two examples of the control tabs for EoS display and fitting, for (a) a high-pressure linear EoS for axis *a*, and (b) a *P*–*V*–*T* thermal-pressure EoS. The buttons for import and export of EoSs are highlighted in part (a).

then typing in the respective parameters. If EoS curve plotting is active, the changes are plotted immediately. This is very useful for illustrating the effects of changing parameter values, especially while teaching.

Alternatively, an *EoSFit7* eos file containing all of the EoS parameters can be loaded from previous calculations or from *EoSFit7*. The different EoSs can be associated with the same groups of data, allowing the fit of different types or different orders of EoS to be compared rapidly, either graphically in the plot window or numerically. The three different EoSs can also be associated with different groups of data, which is useful when analysing data from different experiments or when the data include a phase transition. Two additional buttons on the tab (Fig. 2) allow each EoS to be saved or exported. One output format is an eos file that holds the EoS parameters. This is fully compatible with the *EoSFit7c* program. The second output format is a text file listing all of the calculated properties of an EoS (including the volume or distance, its elastic moduli, and their pressure and temperature derivatives) over a range of pressure and/or temperature chosen by the user. The fixed format of this cal file allows it to be easily read into other programs, such as spreadsheets, for further calculations or for producing all kinds of plots of the EoSs.

When data are present, the EoS parameters can be obtained by estimation or by fitting to the data. The estimation procedure is a very powerful process to obtain good initial values for the EoS using a simulated annealing protocol, and is recommended prior to attempting a least-squares fit of the EoS parameters. Fitting is based on least-squares minimization

of the difference between observed and calculated pressures, not volumes, and uses the same code as *EoSFit7c*. The checkboxes allow the user to select which parameters are refined, and different weighting schemes can be selected if the uncertainties of the data are present in the input data file. The refined EoS is plotted immediately in the graphics window, and the parameter values in the tab are immediately updated. Further details about the refinement results are provided in a pop-up log window (Fig. 3). The parameter values of most

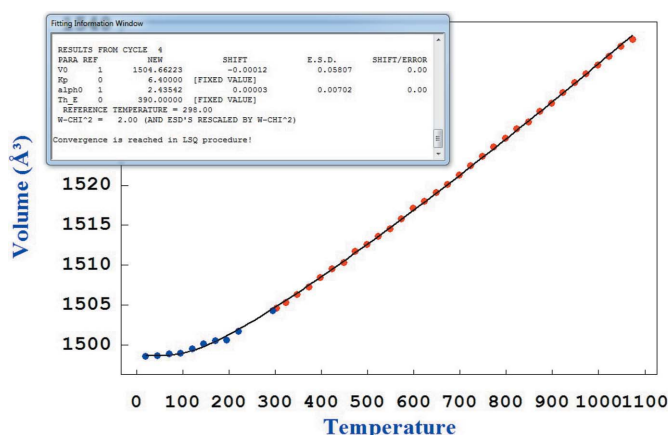


Figure 3

The graphical display in *EoSFit7-GUI* of a fit to the thermal expansion data for the mineral pyrope ($\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}$) from Bosenick & Geiger (1997, blue symbols) and Milani *et al.* (2015, red symbols). The pop-up text box is the log window which contains full information about the least-squares results, including parameter standard uncertainties.

EoSs determined by least-squares fitting are normally highly correlated, and thus the parameter uncertainties alone do not reflect the true uncertainties of the parameters. The best way to visualize the correlations is through plotting the mutual confidence ellipses of pairs of refined parameters (Angel, 2000), and these plots can be readily displayed *via* the ‘V-CV’ button on each tab.

2.3. Plots

The main graphics area occupies the right-hand zone of the GUI (Fig. 1). Icons provide a pop-up dialogue for configuring the graphics pane (line and symbol selection, font faces *etc.*) and options for exporting the graphs. Which experimental data are plotted is controlled by selecting the data groups on the top of the left-hand zone of the GUI (Fig. 1). Multiple EoSs related to the same direction or to the volume can be displayed simultaneously, so that the differences between different fits or different EoS formulae can be seen (Fig. 1). The user can switch rapidly between different types of plot for the same data by selecting the variables (P , V , T , K , K' *etc.*)

from the pull-down menus for the X and Y axes in the ‘Plot’ area at the bottom of the left-hand tabs of the GUI (Fig. 2). This arrangement of controls ensures that the graphics area displays the graphs appropriate for the data type (*e.g.* V or a or b or c) displayed by the tab in the left-hand zone. It also allows the data to be displayed in different ways. For example, it is not possible to determine from visual inspection of the P – V plot which order of the Birch–Murnaghan EoS (Birch, 1947) best describes the compression data of CuCr_2S_4 shown in Fig. 1. However, switching to a plot of normalized pressure against Eulerian strain (Fig. 4*a*) immediately reveals that the fourth-order Birch–Murnaghan EoS is the correct one to describe the data over the entire range of pressure. Plots of the residuals $P_{\text{obs}} - P_{\text{calc}}$ from the least-squares fit of each EoS confirm this conclusion, because the residuals for the second- and third-order fits (Figs. 4*b* and 4*c*) show systematic deviations, whereas the fourth-order EoS fits all of the data within the estimated uncertainties without any pattern in the residuals (Fig. 4*d*). Such residual plots are also useful for detecting the presence of outliers in data sets.

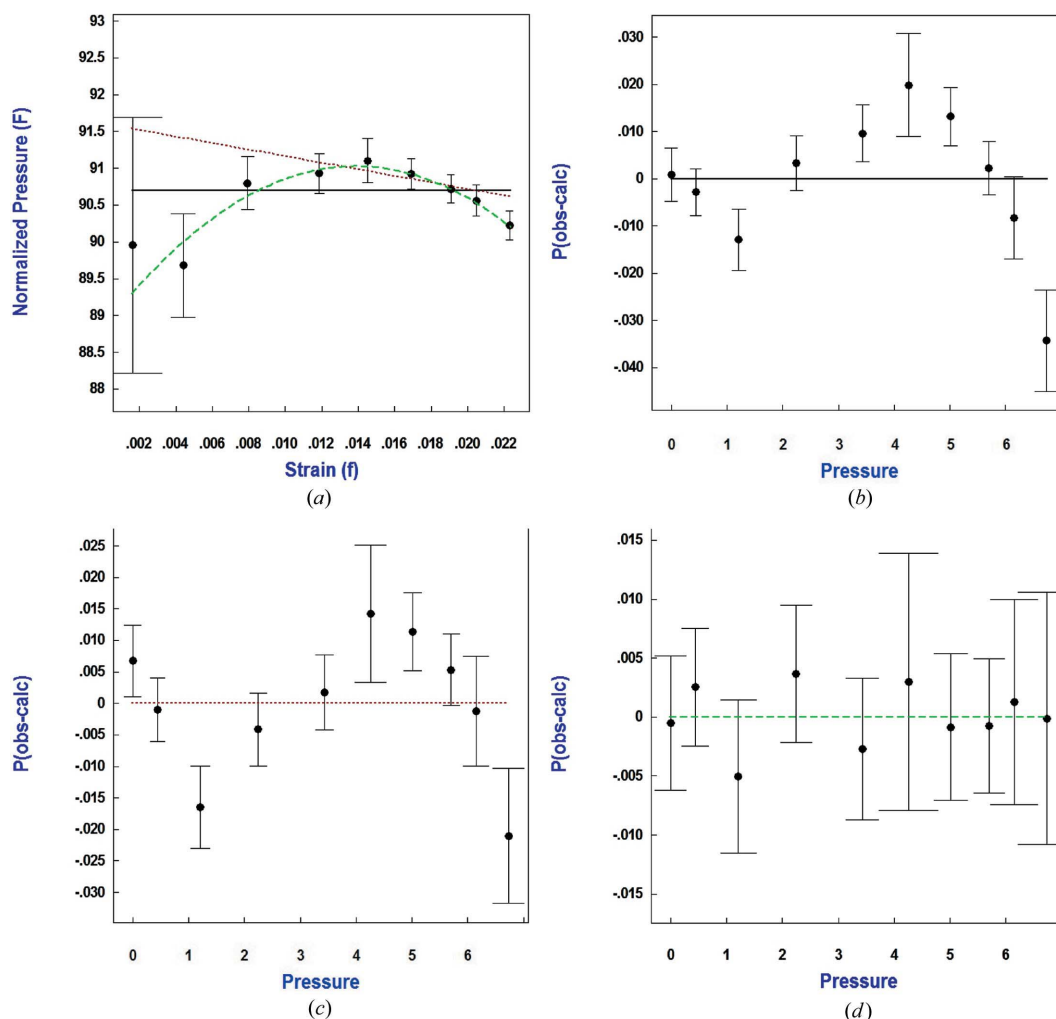


Figure 4

(a) A plot of the normalized pressure (F) versus Eulerian strain (f) for the P – V data of the thiospinel CuCr_2S_4 shown in Fig. 1. This plot clearly demonstrates that the fourth-order Birch–Murnaghan EoS (green) is the most appropriate for describing the data over the entire experimental pressure range. (b)–(d) Plots of $P_{\text{obs}} - P_{\text{calc}}$ after fitting these data with different orders of the Birch–Murnaghan EoS (line colours as in Fig. 1).

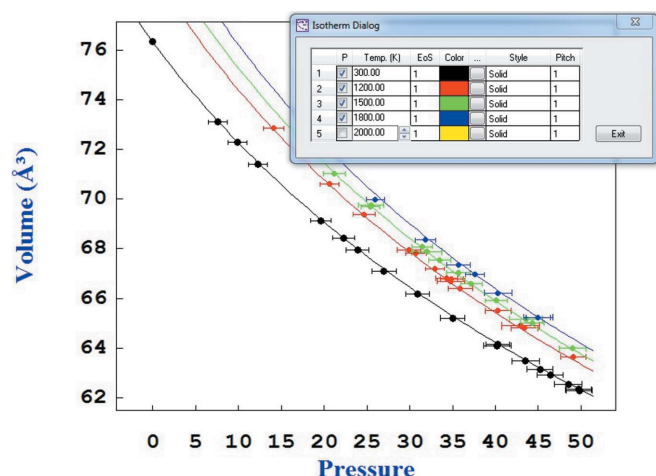


Figure 5

A screen shot of a plot of P - V - T data for ferropericlase (Mao *et al.*, 2011) at temperatures of 300, 1200, 1500 and 1800 K, along with the isothermal P - V curves from a thermal-pressure EoS fit to the data. The additional dialogue box allows the user to plot several isothermal curves for a single EoS, as shown here.

The display of P - V - T data in two dimensions is a challenge. The GUI allows either P or T to be assigned to the X axis for plotting. Normally, volume varies more with pressure than with temperature, so plots with P as the X axis are normally more useful. The user can then plot up to five isothermal compression curves simultaneously (Fig. 5) at temperatures of their choice. If the data are grouped by temperature, then the data points can also be colour coded, making it clear how well the EoS fits each subset of the data. Of course, the individual data groups can also be plotted separately.

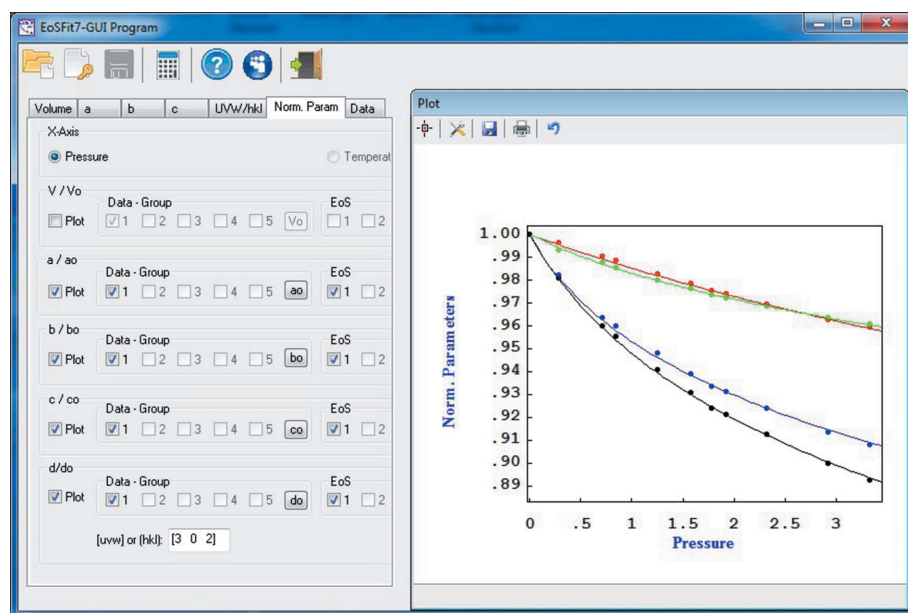


Figure 6

The anisotropy of compression of *catena*-[bis(μ_2 -iodo)-6-methylquinolinecopper(I)] under pressure (Aguirrechu-Comerón *et al.*, 2016) displayed using the 'Norm. Param.' tab of *EoSFit7-GUI*. Measured cell parameters are shown as red, green and blue points. The material is softer in the [302] direction (black dots) than either a or c because of the shear of the unit cell with pressure, which increases the β unit-cell angle.

The left-hand zone includes one further tab, called 'Norm. Param.' (abbreviation for normalized parameters), which is dedicated solely to plotting. While the other tabs allow the plotting of multiple EoSs and multiple subsets of the data all related to either the volume or a single direction, this tab allows the data and multiple EoSs for several directions to be plotted simultaneously. The software automatically normalizes all data to their room-pressure values, so that the plots have V/V_0 or l/l_0 as the Y axis. If desired, the reference values (V_0 or l_0) can be set for each data group on the other EoS tabs, if the room-pressure values are not in the data set. This also allows the user to explore the influence of the reference values on the EoS curves and the f - F plots. The normalized plots provide a direct visual indication of the relative stiffness or softness of the different unit-cell axes. A fourth direction defined by (hkl) or $[UVW]$ can also be plotted, allowing a student to explore visually how compressibility changes with direction in a crystal. For low-symmetry materials, it can also be used to show the effects of large shear strains on the linear compressibilities, and that the compression of the unit-cell axes alone does not necessarily represent the true compressibility tensor. As an example, Fig. 6 shows data for a metal-organic copper(I) iodine complex (Aguirrechu-Comerón *et al.*, 2016) for which the c axis is significantly softer than the a or b axes. However, as a result of the rapid increase in the β angle of the unit cell with pressure, the softest direction is approximately along the [302] lattice vector.

2.4. PV and PVT calculator

This is a separate program that can be installed and used independently from *EoSFit7c* or *EoSFit7-GUI*. It allows the user to perform calculations from a single EoS, to obtain all of the properties of an EoS at any P and T for a P - V - T EoS, or any P for an isothermal EoS. The EoS parameters can be either typed into the GUI directly or loaded from an *EoSFit7* eos file. When the calculator is launched directly from the GUI by using the icon on the program taskbar, the EoS parameters of the current active EoS are loaded automatically into the calculator.

3. Program details

The program was written in Fortran95 using the *CrysFML* (Rodriguez-Carvajal & Gonzalez-Platas, 2003) library, with the *cfml_eos* module (Angel *et al.*, 2014) and the commercial Fortran GUI tool set *Winteracter* (<http://www.winteracter.com>). The program is completely free and is available from <http://www.rossangel.net> for Windows, Linux and MacOS-X operating systems,

together with example data sets and complete help documentation.

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