EosFit v5.2
Users manual

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INTRODUCTION

EosFit started as a program to fit equations of state (EoS) to P,V data. A number of auxiliary programs were subsequently written to perform functions such as the calculation of P at a given V, to produce P-V data sets, and to fit P-V-T data sets. These various programs originally ran on a Vax, and were subsequently ported and further developed in the MS-DOS environment. Version 5.0 was the first integration of these programs into a single package and operates as a command-line interpreter under MS-DOS emulation. It was intended as an intermediate step to a GUI-based system. Version 6.0 is a number of stand-alone GUI's designed for specific calculations, and these will be later combined into a single package to perform fitting, graphing and subsidiary calculations. Versions 5.x and versions 6.x are being developed in parallel.

Version 5.2 was made available on my web site in August 2001. It is not a fully functional version in the sense that not all of the intended commands have been programmed. But it does:

> 1: Fit all of the EoS formulisms listed below
>
> 2: Perform P-V-T fits or just P-V fits
>
> 3: Calculate P from V, or V from P etc
>
> 4: Read variable-format datafiles.

The EosFit programs are distributed on a non-commercial basis and the author would appreciate their use being acknowledged by reference to Angel (2000) in any publications. If you would like to receive program updates (including bug fixes), please register with me as a user by e-mail (rossangelsoftware@gmail.com). If you discover apparent bugs in the program, please send me the *input* file, the *output* file and a full description of the problem by e-mail. Further information will be posted on the web site www.rossangel.com.

1. THE PROGRAM

Installation

Download the eosfit.zip file. It contains the executable, three test datasets and this manual as a *pdf* file.

EosFit5.2 is a single Console-type executable. Copy eosfit.exe to some folder where you keep programs.

EosFit5.2 does not include a file browser. So, you either have to move your datafiles to the directory where the eosfit.exe resides. Or, create a shortcut to the executable in the directory where you want to work. Don't forget to set the working directory of the short-cut to the directory where your datafiles reside (under properties of the short-cut).

Data file format

The datafile is never over-written by the program.

Header Lines: The top of the file can contain a number of lines labelled with title or comment. These lines are ignored by the program, but allow you to annotate the file.

Format Line: The last of these header lines should be the format line. The program reads this line and uses it to interpret the following lines of data. The program recognises the words pressure, volume, temperature, linear, sigp, sigt, sigv and sigl. The use of the "linear" label instead of "volume" indicates that your data is linear (i.e. cell-edge) not volume data. Then use "sigl" for the esd's in the cell edge.

Enter these labels in the order in which your data occur in the following lines.

Data Lines: All lines after the format line are interpreted as data lines. There should be one line for each data point. The order in which the data such as *P*, *V* or *T* appear in each line must be the same. The order is specified by the format line. At minimum you must have either *P* and *V* or *V* and *T*. The uncertainties in *P*, *V* or *T* are optional, but recommended.

Last Line: There is no special end line for the data. The last line of the file must be a data line, not a blank line.

Example: In the left-hand column of the following table are the top lines of the test data file pvttest.dat.

Datafile	Comment
TITLE ORTHOENSTATITE *P,V,T* DATA RESCALED	Title line
Comment This is a test dataset compiled from several sources	Comment line
FORMAT PRESSURE,TEMPERATURE,VOLUME,SIGP,SIGV	Format of following data
0.000,298.0,1.00000,1.000E-6,0.00014 1.395,298.0,0.98754,0.004,0.00013 2.404,298.0,0.97930,0.006,0.00013 2.959,298.0,0.97496,0.007,0.00014 3.528,298.0,0.97090,0.007,0.00013	The data, delimited by commas, one data point per line. Each line has data in the order specified by the format line

Starting the Program

Just click on the shortcut that you have installed in your working directory. You should see:
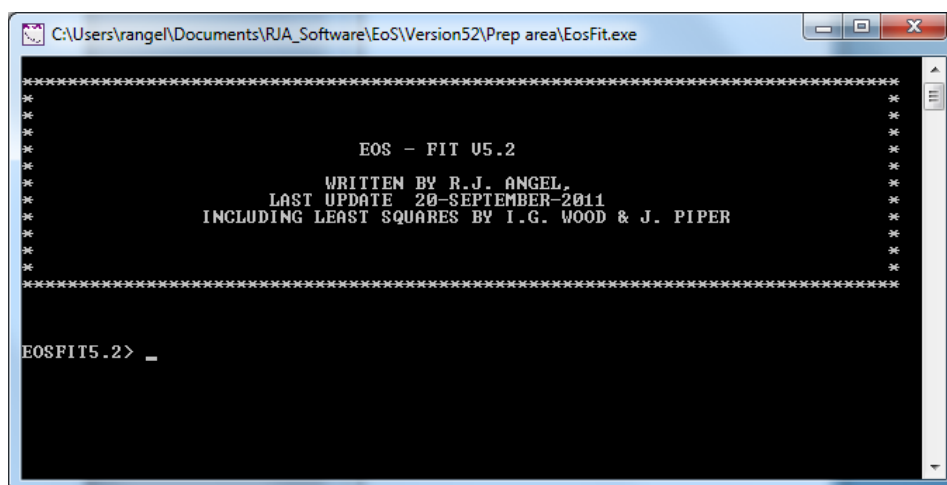
The EOSFIT5.2> prompt is waiting for your input! Input at this level is one of a set of commands. At lower levels within the sub-programs, you will be prompted by questions. The program is not case sensitive!

Command Summary

Not all of the commands and procedures have been written. If you type an unavailable command such as "conf" you will see a message like "call conlev" and control is returned to the command prompt.

Here is a list of the ones that are available. There is a worked example that uses many of these commands later in this manual.

Help provides a listing of all of the commands.
Exit exits from the program.

Read reads in a datafile.
Input allows you to input or change the EoS type and parameters.
Temp allows you to switch between *P,V* and *P,V,T* calculations and to set the reference temperature for *P,V,T*.
List lists the dataset and the calculated *V* if EoS parameters are loaded.
Param lists the current EoS parameters.
Log opens a log file into which the results of least-squares fitting are written.

Pcal calculates the pressure from volume (and temperature).
Vcal calculates the volume from pressure (and temperature).
Fcal calculates *F* and *f* for the EoS or from an input value of *P* and *V*.
Kcal calculates the bulk modulus at a given *P* or *V* (and temperature).
VdP calculates $\int VdP$ between room pressure and a chosen maximum pressure.

PVcal generates a *P,V* dataset from the current EoS parameters and writes it to an ascii file.
FFcal generates a *F,f* dataset from the current EoS parameters and writes it to an ascii file.

Commands can be entered in any order. If the use of a command is inappropriate (for example you try *Pcal* without any EoS parameters) then one of two things will happen. Either you will be returned to the command prompt. Or you will be prompted for additional input.

2. EQUATIONS OF STATE

Formulations

The EoS used in EosFit5.2 most commonly used for fitting isothermal (i.e. *P-V* datasets) are listed briefly here. Further details of the derivations and limitations can be found in, for example, Anderson (1995) and Angel (2001).

Murnaghan. This can be derived from the assumption that the bulk modulus varies linearly with pressure, $K = K_0 + K_0' P$; K_0' being independent of pressure. Integration yields the *P-V* relationship:

$$V = V_0 \left(1 + \frac{K_0' P}{K_0} \right)^{-1/K_0'} \tag{1}$$

This EoS (Murnaghan 1937) both reproduces *P-V* data and yields correct values of the room pressure bulk modulus for compressions up to about 10% (i.e. $V/V_0 > 0.9$), and has the advantage of algebraic simplicity over other formulations such as the Vinet or Birch-Murnaghan EoSs (e.g. Anderson 1995, Angel 2001) which should be used if the range of compression is greater than 10%. The Murnaghan EoS can also be re-arranged to provide a direct expression for pressure in terms of compression:

$$P = \frac{K_0}{K_0'} \left[\left(\frac{V_0}{V} \right)^{K_0'} - 1 \right] \tag{2}$$

Birch-Murnaghan. This is a "Finite strain EoS", and is based upon the assumption that the strain energy of a solid undergoing compression can be expressed as a Taylor series in the finite strain, *f*. The Birch-Murnaghan EoS (Birch 1947) is based upon the Eulerian strain, $f_E = \left[\left(V_0/V \right)^{2/3} - 1 \right] / 2$. Expansion to fourth-order in the strain yields an EoS:

$$P = 3K_0 f_E (1 + 2f_E)^{5/2} \left(1 + \frac{3}{2} (K' - 4) f_E + \frac{3}{2} \left(K_0 K'' + (K' - 4)(K' - 3) + \frac{35}{9} \right) f_E^2 \right) \tag{3}$$

If this EoS is truncated at second-order in the energy then the coefficient of f_E must be identical to zero, which requires that K' has the fixed value of 4 (higher-order terms are ignored). The third-order truncation, in which the coefficient of f_E^2 is set to zero yields a three-parameter EoS (with V_0, K_0 and K') with an implied value of K'' given by (Anderson 1995):

$$K'' = \frac{-1}{K_0} \left((3 - K')(4 - K') + \frac{35}{9} \right) \tag{4}$$

Natural strain. Poirier and Tarantola (1998) developed an EoS based upon the "natural" or "Hencky" measure of linear strain, $f_N = \ln(l/l_0)$ which, for hydrostatic compression, may be

written as $f_N = 1/3 \ln(V/V_0)$. This yields a pressure-volume relationship expanded to fourth-order in strain of:

$$P = 3K_0 \left(\frac{V_0}{V}\right) f_N \left[1 + \frac{3}{2}(K' - 2)f_N + \frac{3}{2}\left(1 + K_0 K'' + (K' - 2) + (K' - 2)^2\right) f_N^2\right] \quad (5)$$

Examination of Equation (5) shows that truncation of this "Natural strain" EoS at second-order in the strain implies a value of $K' = 2$, different from that of the second-order Birch-Murnaghan EoS. For truncation at third-order in the strain, the implied value of K'' is given by:

$$K'' = \frac{-1}{K_0}\left[1 + (K' - 2) + (K' - 2)^2\right] \quad (6)$$

Vinet. The finite-strain EoS do not accurately represent the volume variation of most solids under very high compression ($\eta < 0.6$), so Vinet et al. (1986, 1987a) derived an EoS from a general inter-atomic potential. For simple solids under very high compressions the resulting Vinet EoS provides a more accurate representation of the volume variation with pressure:

$$P = 3K_0 \frac{(1 - f_V)}{f_V^2} \exp\left(\frac{3}{2}(K' - 1)(1 - f_V)\right) \quad (7)$$

where $f_V = (V/V_0)^{1/3}$. There is no theoretical basis for truncation of the EoS to lower order, although examination of Equation (7) shows that such truncation yields an implied value for K' of 1. The value of K'' implied by Equation (7) is given by Jeanloz (1988) as:

$$K'' = \frac{-1}{K_0}\left[\left(\frac{K'}{2}\right)^2 + \left(\frac{K'}{2}\right) - \left(\frac{19}{36}\right)\right] \quad (8)$$

Expansions of the Vinet EoS to include a refineable K'' have been proposed but are not required to fit most experimental P-V data of simple solids. Despite being often called a "Universal EoS" (e.g. Vinet et al. 1986, 1987a) it should be noted that the Vinet EoS is not intended for materials with significant degrees of internal structural freedom such as bond-bending (Jeanloz 1988).

Thermal Equations of State

Within EosFit5.2, P-V-T data is treated with any of the isothermal EoS given above, and by considering the parameters V_0 and K_0 as being the material properties at $P=0$ but at elevated temperature T. The high-temperature value of the zero-pressure volume is:

$$V_0(T) = V_0(T_0) \exp \int_{T_0}^{T} \alpha(T) dT$$

that is derived by integration of the thermodynamic definition of the thermal expansion coefficient $\alpha(T) = V^{-1} \partial V/\partial T$. T_0 is the reference temperature (default value 298 K in the P-V-T calculator, but it can be changed), at which the volume is V_0, and the bulk modulus has the value K_0.

As for the compression of solids, there is no general thermodynamic theory that specifies the form of the function $\alpha(T)$, e.g. Krishnan et al. (1979). At the lowest level of approximation $\alpha(T)$ can be considered a constant, or to vary with linearly with temperature as $\alpha(T) = \alpha_0 + \alpha_1 T$. This

second function is used in EosFit5.2, and leads to the expression for the high-temperature volume at zero pressure as:

$$V_0(T) = V_0(T_0)\exp\left(\alpha_0(T - T_0) + \frac{1}{2}\alpha_1\left(T^2 - T_0^2\right)\right)$$

(9)

With this formulation, the actual values of α_0 and α_1 that describe a *V-T* curve depend on the value of the reference temperature, T_0.

Within the uncertainties of most current experimental measurements, the variation of bulk modulus with temperature can be considered to be linear:

$$K(T) = K_0 + (T - T_0)\left(\frac{\partial K}{\partial T}\right)_P$$

(10)

This formulation, combined with use of a variable K' in the associated isothermal EoS, includes all second derivatives of the volume with respect to the intensive variables *P* and *T*, and is usually sufficient to fit most experimental *P-V-T* data sets collected from room temperature up to ~1000 K. The derivations of thermal EoS more applicable to higher-temperature datasets are given by Duffy and Wang (1998). A simplified extension of the Vinet EoS to variable temperature developed by Vinet et al. (1987b) is only applicable above the Debye temperature.

Units

Equations of state for compression are dimensionless – they can all be re-written in terms of the two ratios K_0/P and V/V_0. Therefore EosFit5.2 makes no assumptions about the units used for the parameters and variables in the compressional parts of the EoS. That is, you must ensure that your units for K_0 and *P* are the same (e.g. both kbar or both GPa), and that the units for V_0 and *V* are the same (e.g. cm^3.mol^{-1}, or Å^3). The value of K' is then dimensionless, and K'' has the units of inverse pressure.

For the temperature parts of the EoS, again there is no internal use of specific units. You can choose any temperature scale (e.g. K or °C or °F). The reference temperature T_0 and the experiment temperature are on this same scale, and the value of the thermal expansion coefficient α is in inverse temperature units. *Important: for ease of display of the small values of α_0 and α_1, they must be entered as, and will be displayed as, multiplied by the factors 10^5 and 10^8 respectively. Thus values of $\alpha(T) = 31 \times 10^{-6} + 2.7 \times 10^{-8}T$ must be entered as $\alpha_0 = 3.1$ and $\alpha_1 = 2.7$.*

Fitting high-pressure lattice parameters

As for volume variations with pressure, there is no fundamental thermodynamic basis for specifying the form of cell parameter variations with pressure. It is therefore not unusual to find in the literature cell parameter variations with pressure fitted with a polynomial expression such as $a = a_0 + a_1 P + a_2 P^2$, even when the *P-V* data have been fitted with a proper EoS function. Use of polynomials in *P* is not only inconsistent, it is also unphysical in that a linear expression implies that the material does not become stiffer under pressure, while a quadratic form will have a positive coefficient for P^2, implying that at sufficiently high pressures the material will expand with increasing pressure. A consistent alternative is provided by using the same EoS as that used to fit the *P-V* data, but substituting the cube of the lattice parameter for the volume in the EoS, and this is the method implemented in the EosFit programs. The data file should

contain the values of the lattice parameters and their esd's indicated by the labels in the format line LINEAR and SIGL. The cubing of the lattice parameter and the transformation of it's esd is performed by the program. The refined parameter value and its esd is transformed back from volume to unit-cell parameter, but note that the printed variance-covariance matrix contains entries for the lattice parameter cubed. Note also, that the value of "K_0" obtained from fitting the cell parameters in this way is related to the zero-pressure compressibility β_0 of the axis by $-1/3K_0 = \beta_0 = a_0^{-1}(\partial a/\partial P)_{P=0}$ in which a_0 is the length of the unit-cell axis at zero pressure.

For crystals with higher than monoclinic symmetry the definition of the axial compressibilities in this way fully describes the evolution of the unit-cell with pressure because the tensor describing the strain arising from compression is constrained by symmetry from rotating. In the monoclinic system, however, one unit-cell angle may change, and in triclinic crystals all three unit-cell angles may change. The full description of the change in unit-cell shape in these cases must therefore include the full definition of the strain tensor resulting from compression. A computer program, originally written by Ohashi (1972) is available to calculate the components and principal axes of strain tensors. The calculation method of Ohashi (1972), further developed by Schlenker et al. (1975) and Jessen and Küppers (1991), is explicitly based upon a finite difference approach. The strain is evaluated from the change in lattice parameters between one data point and the next. Thus the resulting strain tensor represents an average strain over this interval in pressure or temperature. This is a sound approach for crystals of orthorhombic symmetry, or higher, because the orientation of the strain ellipsoid is fixed by symmetry. But for triclinic and monoclinic crystals the strain ellipsoid may rotate with changing P or T. The finite difference calculation of strain then represents an average not only the magnitudes of the principal axes of the strain ellipsoid, but also an average of their orientation over the finite interval in P or T. An alternative approach which avoids this problem and employs the calculation of the continuous derivatives of the unit-cell parameters with respect to T (or P) has been developed by Paufler and Weber (1999).

Fortunately, in monoclinic systems the strain tensor often does not rotate significantly with pressure. Then it may be appropriate to fit quantities such as $a$sinβ against pressure with an EoS function, or the β angle separately as a polynomial function of pressure (e.g. Angel et al. 1999). The important criterion is that the resulting expressions provide not only a good fit to the data, but are reliable in extrapolation to further pressures of interest (e.g. when studying phase transitions; see Angel 2000). The reliability of these extrapolations can always be tested by parallel calculations with different functions (e.g. Boffa-Ballaran et al. 2000). A further internal check on the robustness of the extrapolations can be obtained by comparing the unit-cell volumes obtained from the lattice parameters extrapolated to a given pressure with those predicted by the EoS function fitted to the unit-cell volume.

3. USING EosFit5.2 – A WORKED EXAMPLE

Because of the algebraic form of EoSs, least-squares fitting of *P-V* data leads to high correlations between the refined parameters V_0, K_0 and K'. Great care must therefore be taken in fitting EoS to avoid unintended bias of the resulting parameters by incorrect weighting schemes, incorrect fixing of parameters or outliers in the dataset. And in assessing the final refined parameter values the covariance must be considered. Further details about the methods of data analysis and assessment of the results are provided in Angel (2001). Here the fitting of a *P-V* dataset (Table 1) is used to illustrate the use of EosFit5.2.

Because all of the EoS listed above, except the Murnaghan, can be written with pressure as a function of volume and not *vice-versa*, the EosFit5.2 program performs least-squares fit of *P-V* data with pressure as the dependent variable.

Assignment of weights. In any *P-V* dataset, both the pressures and the volumes have experimental uncertainties associated with them. EosFit5.2 provides the user with the opportunity to perform the least-squares fit with either the data un-weighted, or with weights derived from either the estimated uncertainties in the pressures, or in the volumes, or both. If one or both uncertainties are not present in the datafile, then the choice of weighting scheme is restricted by the program. Uncertainties in volumes are converted into uncertainties in pressure by the effective variance method (e.g. Orear 1982):

$$\sigma^2 = \sigma_p^2 + \sigma_V^2 \cdot \left(\frac{K}{V}\right)^2$$
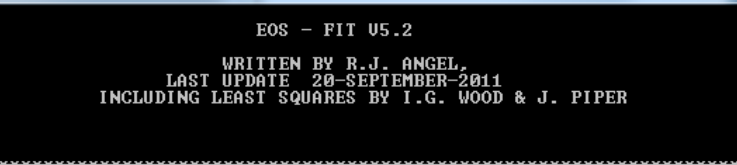
Because the bulk modulus at the pressure of each datum appears on the right-hand-side of this equation, the EosFit5.2 program recalculates the weights before each least-squares cycle.

Refinement strategy. Examination of the equations of all isothermal EoS (Eqns. 1-8) shows that they are non-dimensional; they can all be written in terms of P/K_0 and V/V_0 Therefore K_0 and V_0 have the same units as the experimental pressures and volumes respectively and are the scaling parameters of an EoS. In particular, V_0 is a quantity that is dependent upon the calibration of the technique used to measure the volumes. For example, in monochromatic angle-dispersive powder diffraction, the volumes obtained from fitting the powder pattern will depend upon the alignment of the monochromator and the value of the resulting X-ray wavelength. Errors in calibration of the sample-to-detector distance will also strongly affect the value of V_0. Similarly, in energy-dispersive diffraction the volume is dependent upon the energy calibration of the detector. In all of these cases the volumes measured at high pressures may be on a different scale from some high-accuracy value of V_0 determined by another technique. As demonstrated by Hazen and Finger (1989), the fixing of V_0 to such an inappropriate value can lead to incorrect estimates of the other EoS parameters being obtained from the least-squares refinement to high-pressure volume data.

The parameters V_0 and K_0 thus have the largest influence on the calculated pressure and should always be refined. For isothermal data sets the first stage of refinement should therefore be the refinement of V_0 and K_0 alone in a second-order EoS, with the next higher order term, K' set to its implied value. For fitting the quartz data in Table 1 with a Birch-Murnaghan EoS, we proceed as follows with the EosFit5.2 program (a summary of the results that you should obtain is given in Table 2).

Running the refinement. Install a shortcut to eosfit.exe in the directory in which the test datafile (quartzpv.dat) is stored (see Installation).

Double-click on the shortcut, you should see the following:
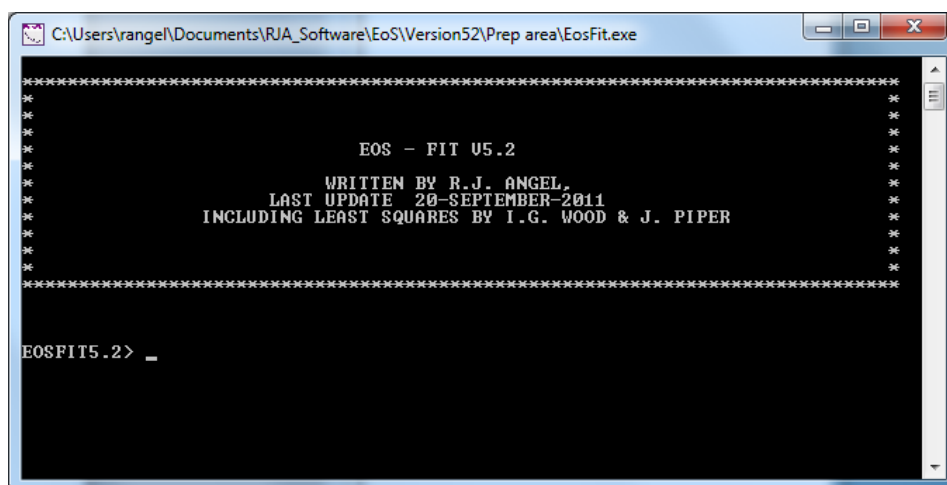
At the command-line prompt, type ***read*** and then enter the name of the datafile, quartzpv.dat:

Type ***list*** to obtain a list of the data. After one page of output you have to hit a <CR> to obtain a listing of the last datapoints. Note that there are no entries for the columns PCALC or DELTA-P, because you have not yet entered any EOS parameters.

Type ***input*** to choose an EoS formulism to use and to input the EoS parameters. The dataset is *P-V* data, so answer ***0*** to the first question, and select a Birch-Murnaghan EoS (***2***) of third order (***3***). Then enter the values ***113.0, 40.0, 4.0*** for the EoS parameters. The screen should now look like this:

Type *list* again to obtain a list of the data with calculated pressures listed. This provides you with a way in which to check that the starting parameters for the least-squares process are approximately correct. If the DELTA-P values get too big, the least-squares will fail.

Start the least-squares process by typing *fit*. After entering a name for a log file (to which all the results are printed) the type and parameters of the EoS are listed. If these are not correct, typing *y* to the question Do you want to change these values? enables you to input new values.

You now choose which parameters to refine at the next list by entering *y* or *n*. Start by refining just V_0 and K_0, but not Kp.

The next prompt allows you to select the weighting scheme applied in the least-squares fitting. The choices are dependent upon which uncertainties are present in the datafile. In this example we have both esd(P) and esd(V). Therefore we will use both in this refinement: enter *y* to both questions Use in weights?

After answering the last question, the least-squares runs until convergence and the results of the final refinement cycle are reported to the screen:

You can see at the top of this image the inputs for the least-squares controls, and at the bottom are listed the refined parameters. In this list the columns from left to right are:

- parameter name,
- a flag =1 for refined parameter, 0 for not refined,
- the value of the parameter,
- the shift in this value in the last cycle,
- the estimated standard deviation of the parameter value (increased by χ^2_w if it is greater than 1.0),
- the shift in the last cycle divided by the esd (should be zero at convergence).

Note that unrefined parameters and the implied value of the next highest parameter in the EoS are also listed.

Enter a <CR> to obtain a list of the observed and calculated pressures at each data point, a second <CR> to get the second page of this list, and then a third <CR> to obtain the parameters describing the quality of fit:

Note the large value of 128 for χ^2_w, together with the maximum misfit, $\left| P_{obs} - P_{calc} \right|_{max}$, labelled "Maximum Delta-Pressure" more than ten times larger than the esd in an individual data point. This indicates that this EoS does not represent the data. The EoS must therefore be expanded by

a further parameter by refining *K*p as well. This can be achieved by answering **y** to UPDATE EOS PARAMETERS (Y/N)? which stores the refined parameters and then **y** to FURTHER CALCULATIONS (Y/N)?

You now have the opportunity to change the parameter values (but don't do it), and then you should choose to refine the value of *K′* as well as V_0 and K_0. Select both weighting options as before and you will obtain:

This expansion of the EoS to third-order reduces χ^2_w to 0.95, indicating a significant improvement to the fit. The same conclusion would be drawn from the other indicators; the refined value of the additional parameter *K′* (5.99) differs by 50 esd's from the previously implied value of *K′* = 4, the esd's of V_0 and K_0 have decreased, the maximum misfit is similar to the estimates of the uncertainties in pressure estimated directly from the experiment, and the value of V_0 is identical to that determined experimentally.

As a final step, proceed through the listings and questions again until you reach:

Enter *y*, select *P-V* data, and a fourth-order Birch-Murnaghan EoS. You could now change the parameter values, but leave them as they are because they already represent a good fit to the data.

Now refine a fourth-order Birch-Murnaghan EoS by setting all of the refinement flags to *y* so as to refine the value of *K″*:
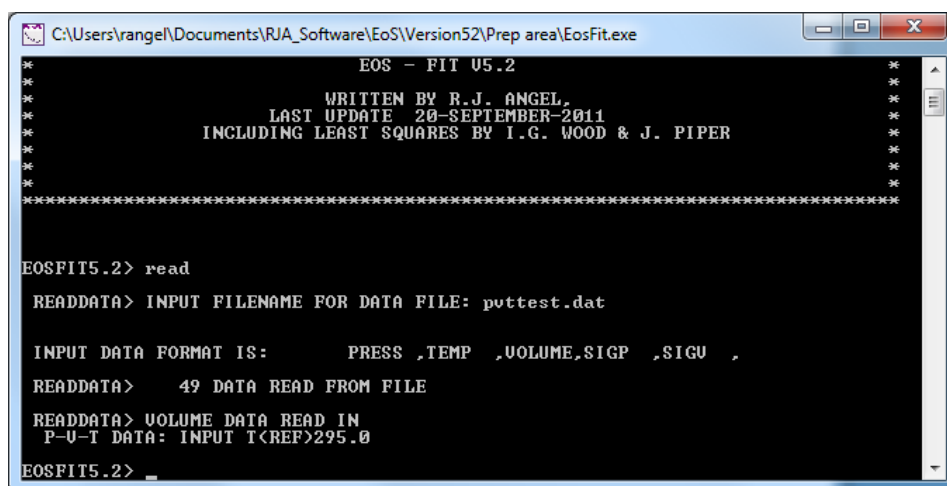

This refinement yields only a marginal improvement in χ^2_w, because the refined value of *K″* only differs marginally (1.2 esd's) from the value implied by the 3rd-order truncation of the EoS. Note also that the esd's of K_0 and *K′* have increased significantly in this last refinement due to their strong correlation (93.6% and -99.2% respectively) with *K″*. For practical purposes, therefore, the 3rd-order Birch-Murnaghan EoS would be considered to yield an adequate representation of the data-set.

The steps in the refinement of the Natural Strain EoS to the same data-set (Table 2) are similar, except for the choice of termination of the refinement process. In this case further expansion of the Natural Strain EoS to 4th order results in a significant decrease in χ^2_w from 1.15 to 0.93 as a result of the value of *K″* deviating by more than 4 esd's from the value implied by the 3rd-order truncation (Eqn. 6).

If at any point you enter **y** to UPDATE EOS PARAMETERS (Y/N)? and then exit to the command prompt, the parameters from the fit will be used as the default in all calculations unless you choose to change them. They are also used to calculate PCALC when you type **list**.

PVT fitting. The file pvttest.dat contains a *P-V-T* dataset for orthoenstatite, compiled from many sources in the literature, with temperature in Kelvin. When you first read in the dataset to EosFit5.2 you will be prompted for the reference temperature:

```
*                 EOS - FIT V5.2                    *
*                                                    *
*                 WRITTEN BY R.J. ANGEL,             *
*            LAST UPDATE  20-SEPTEMBER-2011          *
*         INCLUDING LEAST SQUARES BY I.G. WOOD & J. PIPER   *
*                                                    *
*                                                    *
*                                                    *
********************************************************

EOSFIT5.2> read

 READDATA> INPUT FILENAME FOR DATA FILE: pvttest.dat

 INPUT DATA FORMAT IS:       PRESS ,TEMP  ,VOLUME,SIGP  ,SIGV  ,

 READDATA>    49 DATA READ FROM FILE

 READDATA> VOLUME DATA READ IN
  P-V-T DATA: INPUT T<REF>295.0

EOSFIT5.2> _
```
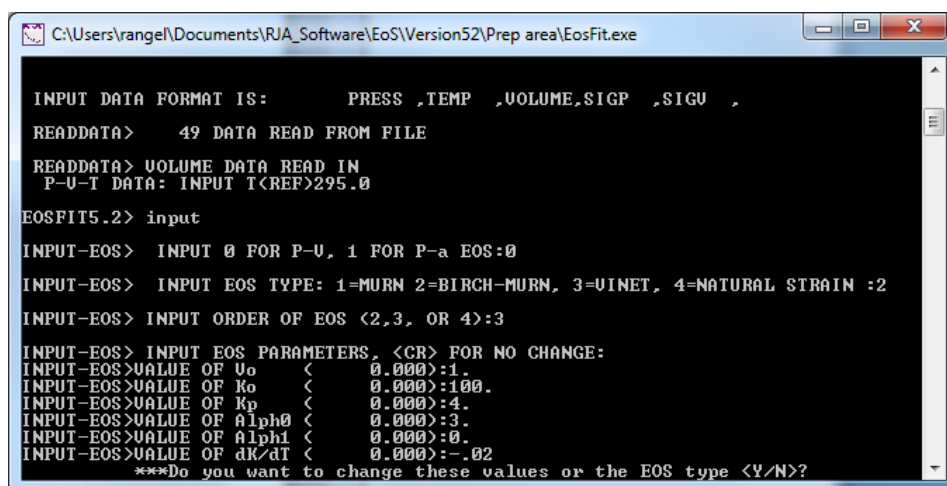
The reference temperature can be changed by the command *temp*. Remember that the actual refined values of the thermal expansion coefficients α_0 and α_1 as well as V_0 and K_0 that describe a dataset will depend on the value of the reference temperature, T_0.

The input and output from the program is adjusted when you have temperature-data so that you can enter and read the necessary parameters and values. For example, here is the result of typing *input*, along with some suggested starting values for fitting the dataset pvttest.dat:

```
 INPUT DATA FORMAT IS:       PRESS ,TEMP  ,VOLUME,SIGP  ,SIGV  ,

 READDATA>    49 DATA READ FROM FILE

 READDATA> VOLUME DATA READ IN
  P-V-T DATA: INPUT T<REF>295.0

EOSFIT5.2> input

INPUT-EOS>  INPUT 0 FOR P-V, 1 FOR P-a EOS:0

INPUT-EOS>  INPUT EOS TYPE: 1=MURN 2=BIRCH-MURN, 3=VINET, 4=NATURAL STRAIN :2

INPUT-EOS> INPUT ORDER OF EOS <2,3, OR 4):3

INPUT-EOS> INPUT EOS PARAMETERS, <CR> FOR NO CHANGE:
INPUT-EOS>VALUE OF Vo    (      0.000):1.
INPUT-EOS>VALUE OF Ko    (      0.000):100.
INPUT-EOS>VALUE OF Kp    (      0.000):4.
INPUT-EOS>VALUE OF Alph0 (      0.000):3.
INPUT-EOS>VALUE OF Alph1 (      0.000):0.
INPUT-EOS>VALUE OF dK/dT (      0.000):-.02
          ***Do you want to change these values or the EOS type <Y/N>?
```

And this is the result of a weighted refinement to the data:

Linear fitting. The file quartza.dat contains a dataset of the *a* unit-cell edge of quartz from Table 1. When loading data or inputing parameters with linear data make sure that you do select the linear data option, as in the second line in this image:

Table 1. Cell parameters of quartz with pressure, from Angel et al. (1997)

P: GPa	a: Å	c: Å	V: Å^3
10^{-4}	4.91300(11)	5.40482(17)	112.981(2)
0.429(9)	4.89295(29)	5.38861(22)	111.725(14)
0.794(10)	4.87657(12)	5.37563(12)	110.711(6)
1.651(9)	4.84201(15)	5.34856(14)	108.597(7)
1.845(9)	4.83461(39)	5.34284(37)	108.150(19)
1.933(9)	4.83136(17)	5.34135(17)	107.974(8)
2.628(12)	4.80593(16)	5.32266(15)	106.467(8)
3.299(9)	4.78306(18)	5.30679(16)	105.141(9)
3.468(12)	4.77750(27)	5.30341(22)	104.831(12)
3.778(12)	4.76798(22)	5.29692(22)	104.285(10)
4.026(12)	4.75970(27)	5.29116(28)	103.810(13)
4.553(11)	4.74411(16)	5.28128(14)	102.939(7)
4.827(14)	4.73671(25)	5.27699(23)	102.534(12)
5.212(11)	4.72561(21)	5.27072(19)	101.933(10)
5.416(12)	4.71973(17)	5.26617(17)	101.592(08)
5.736(11)	4.71137(25)	5.26150(21)	101.143(11)
6.203(14)	4.69710(32)	5.25385(32)	100.385(15)
6.478(13)	4.69089(33)	5.25027(30)	100.051(15)
6.751(12)	4.68392(18)	5.24622(20)	99.677(09)
7.191(15)	4.67228(27)	5.23993(21)	99.064(12)
7.898(8)	4.65612(30)	5.23058(28)	98.204(14)
8.449(15)	4.64333(15)	5.22416(32)	97.545(16)
8.905(13)	4.63253(38)	5.21863(35)	96.989(17)

Table 2. EoS parameters fitted to the quartz P-V data of Angel et al. (1997)

	V_0 : Å^3	K_0 : GPa	K'	K'' : GPa^{-1}	χ^2_w	$\left| P_{obs} - P_{calc} \right|_{max}$: GPa
BM2	112.97(2)	41.5(3)	[4.0]	[-.094]	128	0.32
BM3	112.981(2)	37.12(9)	5.99(5)	[-.265]	0.95	0.025
BM4	112.981(2)	36.89(22)	6.26(24)	-.41(12)	0.93	0.026
NS2	112.95(5)	46.5(6)	[2.0]	[-.022]	580	0.65
NS3	112.982(2)	36.39(11)	6.91(7)	[-.825]	1.15	0.026
NS4	112.981(2)	36.90(24)	6.25(29)	-.39(11)	0.93	0.026
Vinet	112.981(2)	37.02(9)	6.10(4)	[-.319]	0.90	0.025
Murn.	112.981(2)	37.63(10)	5.43(4)	[0]	1.57	0.033

Note: Numbers in parentheses represent esd's in the last digit. Numbers in square brackets are the implied values of the parameters.

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