

# **High-Pressure Powder Diffraction**

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## **INTRODUCTION**

Diffraction studies at high pressures provide an opportunity to probe the behaviour of the chemical bonding of solids as a function of decreasing inter-atomic separation, without the complications introduced by changing chemistry. In this contribution to the workshop, the methods available for performing high-pressure powder diffraction are briefly introduced along with a number of important cautions for the experimentalist new to high-pressure diffraction.

In general, powder diffraction methods at high pressures yield data that is of lower quality than that which is obtainable from the same sample measured at ambient conditions on the same instrument. The reasons for this are several. High-pressure apparatus generally only allow small sample volumes while the containment of the sample absorbs both the incident and diffracted beams, all of which reduce the intensities of the diffracted beams. Secondly, the containment of the sample can give rise to scattered radiation that appears as background in the detector, either by diffraction from pressure-cell components (especially the gasket) or other scattering processes including Compton scattering from the diamonds of diamond-anvil cells (DACs). The lower signal levels can only be overcome by longer counting times and more intense radiation sources. The higher levels of background are best addressed by appropriate shielding and/or collimation at the time of the experiment.

Thus, the most important differences between performing a powder diffraction experiment at high pressure and one at ambient conditions are in the data collection process. Some important points are reviewed here in some detail. Then, a few brief remarks are made about the refinement of high-pressure powder diffraction data, which is essentially no different from refinement of data collected at ambient conditions. Finally, a brief review of how to analyse pressure-volume data in the form of Equations of State (EoS) is presented, along with a program to do the necessary least-squares fitting.

## **EXPERIMENTAL METHODS**

*X-ray powder diffraction.*

Synchrotrons have been the X-ray source of choice for some time for high-pressure powder diffraction, which can be performed, with care, to pressures in excess of 100 GPa. A wide variety of diamond-anvil cell designs have been developed for high-pressure powder diffraction, but many are based on the very simple principle of applying a moderate force to the relatively large surface-area of the thread of a drive screw, and then transferring this force onto the small area of the tips of two opposed diamond-anvils. An alternative drive mechanism is used in the “gas-membrane cells”, in which the force is generated by inflating a metal membrane whose expansion drives the anvils together. DACs that have been specifically designed for single-crystal diffraction can also be successfully used for powder diffraction. An extensive review of DAC designs, including their relative advantages and disadvantages, can be found in Hazen (2000).

Most early X-ray powder diffraction studies at high pressures employed energy-dispersive diffraction, a method which is limited in resolution because of the restricted energy resolution of the solid-state detectors involved. The advent of image-plate detectors and improved DAC designs with larger opening angles to allow X-ray access to the sample has resulted in angle-dispersive diffraction becoming the standard method. The data quality from image plates is also greatly increased because the entire diffraction cone can be collected and therefore effects due to, for example, sample texture can be readily identified before integration of the data into a conventional 1-dimensional Intensity vs.  $2\theta$  data-set used for refinement. Currently, data quality is such that reliable unit-cell parameters can be obtained from high-pressure powder diffraction as well as structural data in more simple systems. The recent introduction of in-situ read-out from image plates that allows data to be collected and processed on a  $\sim 1$  minute cycle (Thoms et al., 1998) makes these detectors competitive with other area detectors such as CCD-based systems for real-time studies of phase transitions, and rapid measurements of compressibility.

### ***Neutron powder diffraction.***

Neutron diffraction is the method of choice for studies of materials containing both light and heavy atoms. For precise studies up to 0.5 GPa there are a wide variety of gas-pressure cells suitable for both angle-dispersive and time-of-flight diffraction. For slightly higher pressures there are a variety of clamp cells, the latest developments of which can reach pressures of 3.5 GPa and temperatures in excess of 800 K (e.g. Knorr et al. 1997, 1999). Scaled-up opposed-anvil cells equipped with sapphire anvils have been used to pressures of at least 3 GPa (e.g. Kuhs et al. 1996). For higher pressures there is the Paris-Edinburgh cell which is capable of developing pressures of up to 25 GPa (Besson et al. 1992, Klotz et al. 1998).

### ***Pressure Media***

It is very important to perform high-pressure diffraction experiments under well-defined conditions of applied stress. In effect, this means that a hydrostatic pressure medium must be used to enclose the crystal, because non-hydrostatic stresses in a high-pressure device are very difficult to quantify. The effects of non-hydrostatic stresses include, but are probably not limited to -

- Broadening of diffraction peaks and consequently reduction in signal-to-noise ratios.

- Incorrect measurement of pressures (see the example of the ruby pressure sensor, below).

- Displacement of the transition pressures of ferroelastic or coelastic structural phase transitions (e.g. Decker et al. 1979).

A 4:1 mixture by volume of methanol:ethanol remains hydrostatic to just over 10 GPa (Eggert et al. 1992) and is convenient and suitable for many studies. If the sample dissolves in alcohols, then a mixture of pentane and iso-pentane which remains hydrostatic to ~ 6 GPa (Nomura et al. 1982), or a solidified gas such as N<sub>2</sub>, He, or Ar can be employed. Water appears to remain hydrostatic to about 2.5 GPa at room temperature, just above the phase transition from ice-VI to ice-VII (Angel, unpublished data). The solid pressure media such as NaCl or KCl favoured by spectroscopists are very non-hydrostatic even at pressures below 1 GPa. Similarly, the “fluorinert” material used in many neutron diffraction experiments because of its low neutron scattering power becomes significantly non-hydrostatic at ~1.3 GPa. At pressures in excess of the hydrostatic limit of the solidified gas and fluid pressure media, the non-hydrostatic stresses can be relaxed after each change in pressure by annealing the sample chamber, either by laser-heating or an external resistance furnace. For example, heating a cell in which the ethanol:methanol mixture is the pressure fluid to 150-200 °C for about 1 hour is sufficient to relax the non-hydrostatic stresses developed above 10 GPa (Sinogeikin and Bass, 1999).

Ideally each grain of the sample should be completely surrounded by the pressure fluid, and not make contact with any other grain because grain-grain contacts can lead to the development of non-hydrostatic stresses. This criterion can not be achieved perfectly, except by resort to a single-crystal experiment! But in loading a high-pressure cell for powder diffraction, it is important not to over-fill the sample chamber with sample - for DACs and X-ray diffraction the author’s experience is that the lightly-compressed powder should occupy approximately one-half of the volume of the hole in the gasket.

### ***Pressure Measurement***

The ruby fluorescence method is the most commonly used to determine pressure in diamond-anvil cell measurements. It is based upon the observation that a pair of electronic transitions in the Cr<sup>3+</sup> dopant atoms in Al<sub>2</sub>O<sub>3</sub> change in energy as the Al<sub>2</sub>O<sub>3</sub> lattice is compressed. The fluorescence in the red area of the optical spectrum is strong and easily excited by blue/green laser light, and the shift is quite large, approximately 3.6Å/GPa. Unfortunately, the fluorescence wavelength is also very sensitive both to temperature, such that a 5° temperature change gives rise to a shift equivalent to 0.1 GPa (Barnett et al. 1973, Vos and Schouten 1991). It is also sensitive to the *c/a* ratio of the Al<sub>2</sub>O<sub>3</sub> host lattice (Sharma and Gupta 1991). As a result, non-hydrostatic stresses increase the observed shift of the stronger R<sub>1</sub> component of the doublet, and can yield an apparent pressure that is higher than the true pressure (Gupta and Shen 1991, Chai and Brown

1996). Other fluorescence sensors have also been employed; for reviews see Holzapfel (1997) and Miletich et al. (2000). Measurement of optical fluorescence is relatively fast, and is extremely useful for setting the approximate pressure in a DAC prior to a diffraction measurement. With the proper precautions it can yield pressures as precise as 0.1 GPa, provided temperature fluctuations are completely excluded. In reality, these and other factors often mean that 0.3 GPa is a more realistic estimate of the precision. For more precise pressure determination internal diffraction standards can be used in DACs, while this is essential for completely enclosed cells, such as the Paris-Edinburgh cell. The pressure is then determined from the unit-cell volume of the standard and its EoS. The precision in pressure then depends upon the precision of the volume measurement and the bulk modulus of the material; the softer the standard the more precise the pressure determination. Materials in common use as standards at pressures up to 10 GPa include NaCl (Brown 1999), quartz (Angel et al. 1997) and fluorite (Hazen and Finger 1981, Angel 1993), while metals such as gold (e.g. Heinz and Jeanloz 1984) have been used at higher pressures. It is important to note that there is no absolute pressure standard measurement above 2.5 GPa, so all EoS and all pressure scales are provisional and subject to revision in the light of improved calibrations. As an example, the pressure scale based upon the EoS of NaCl which was introduced by Decker (1971) and developed by Birch (1986) was recently shown to be in significant error by Brown (1999).

### *Experimental Strategy.*

Because all pressure cells affect the intensities in the diffraction pattern of the sample, and imperfect alignment and positioning of the cell with respect to the incident beam and the detector can influence the positions of the diffracted beams, it is strongly recommended that all high-pressure studies should commence with a measurement of the diffraction pattern of the sample in the pressure cell, but at ambient pressure. Comparison of the result with a refinement of the diffraction pattern measured outside of the cell will provide an indication of the systematic errors present in the high-pressure results. For EoS determination, the room pressure determination of the unit-cell volume also provides a strong constraint on the EoS parameters. In all subsequent analysis, the room pressure datum collected from within the cell should be used as the room-pressure reference. Use of data collected outside of the cell as this reference often leads to false conclusions being drawn about the high-pressure evolution of structure or unit-cell parameters (e.g. Hazen and Finger, 1989).

If the only intention of the experiment is to derive the parameters of the EoS of the sample, then the number of data points required to obtain a given precision in the EoS parameters can be estimated from the known experimental parameters. The details are given in Angel (2000a). To summarise, the number of data required can be estimated from the bulk modulus of the sample (usually known approximately, or can be estimated), the precision of the volume and pressure measurements and the maximum pressure achievable.

## **REFINING HIGH-PRESSURE POWDER DIFFRACTION DATA**

As noted above, the refinement of powder-diffraction data by the Rietveld method is not intrinsically different from the refinement of data collected under any other conditions. Just a few notes are given here, based on the author's own, but somewhat limited, experience.

The reduction of the data collected by the detector, whether time-of-flight neutron powder diffraction data or a 2-dimensional image from an area detector used in X-ray powder diffraction, is usually performed by software provided by the facility. This data reduction usually includes, if appropriate, corrections for spatial distortion and calibration of the detector (e.g. Fit2D, Hammersley et al. 1995, 1996) and normalisation to the incident beam spectrum. An important consideration for X-ray powder diffraction is the calibration of the wavelength and the sample-to-detector distance, normally obtained by performing diffraction from a standard sample. Repeat measurements of the standard over the period of the experiment will provide an estimate of the reproducibility and variation of these parameters.

Because the background levels in a high-pressure diffraction pattern are much higher than in an ambient pressure measurement, the question of whether the background should be subtracted before refinement rears its ugly head. The statistical arguments for and against such a process have been made before in the literature. My personal view is that the background should be fitted as far as possible, although specific regions in which the background changes sharply may be excluded entirely from the fitting process. Within GSAS, the best background function for most high-pressure data appears to be the shifted-Chebyshev polynomial. For some cases, the refinement becomes more stable if a set of fixed background points are determined to provide a basis for the refinement process. Diffraction peaks from the cell components can either be excluded (if they are few and they do not interfere with the sample), or they can be refined as further phases. If these phases are refined, it is quite normal to have to resort to a Le-Bail fit to obtain a reasonable approximation to the observed intensities, as one expects cell components to have strong preferred orientation and possibly an exceedingly poor powder average. The same cautions apply to the diffraction pattern from the sample itself, especially as the application of pressure can often lead to the development of strong preferred orientation. Lastly, the peak widths of the samples should be monitored carefully from pattern to pattern in order to detect the possible onset of non-hydrostatic conditions. However, this is not a guaranteed test for non-hydrostatic conditions as it is possible that these can affect a pressure sensor such as ruby at pressures *below* that at which broadening is first detected in the sample.

In summary, refinements of high-pressure data should, at minimum, include refinement of the background, together with the unit-cell parameters, scale factors and peak-widths of each phase in the sample. If image-plate data is being fitted, the  $2\theta$  zero of the pattern should also be refined as the integration methods do not locate this to better than about 1 pixel in the 2-dimensional image. Refinement of further parameters, including structural parameters, depends on the quality of the pattern.

## EQUATIONS OF STATE

### *Formulations of Equations of State.*

The unit-cell parameters and unit-cell volume of a solid normally vary in a non-linear way with pressure because as the volume of the solid becomes smaller the inter-atomic forces opposing further compression become stronger. The “stiffness” of a solid is characterised by the bulk modulus, defined as  $K = -V \partial P / \partial V$  which will generally increase with increasing pressure. Different assumptions can then be made about how  $K$  varies with  $P$ , or how  $V$  varies with  $P$ . Each set of assumptions then leads to a relationship between  $P$  and  $V$  known as an “Equation of State” or EoS. Note that, unlike “ideal gases” there is no absolute thermodynamic basis for specifying the correct form of the EoS of solids, although for simple solids such as the NaCl structure a direct relationship between the inter-atomic potential and the EoS can be derived (see Anderson 1995 for a thorough review).

Measured equations of state are usually parameterized in terms of the values of the bulk modulus and its pressure derivatives,  $K' = \partial K / \partial P$  and  $K'' = \partial^2 K / \partial P^2$ , evaluated at zero pressure. These zero-pressure moduli are normally denoted by a subscript “0”, thus:  $K_0 = -V_0 (\partial P / \partial V)_{P=0}$ ,  $K'_0 = (\partial K / \partial P)_{P=0}$ , and  $K''_0 = (\partial^2 K / \partial P^2)_{P=0}$ . High-pressure diffraction measurements are isothermal measurements, so in the following all references to bulk modulus,  $K_0$ , and its derivatives  $K'_0$  and  $K''_0$ , refer to isothermal values and all compression values,  $\eta = V/V_0$ , and variables such as finite strain  $f$  derived from them, are similarly isothermal quantities. The relationship between the isothermal bulk modulus, more generally denoted  $K_T$ , and the adiabatic bulk modulus  $K_S$  that describes compression in a thermally closed system (at constant entropy) is  $K_S = K_T (1 + \alpha \gamma T)$  where  $\alpha$  is the volume thermal expansion coefficient and  $\gamma$  is the Gruneisen parameter. At room temperature the factor  $\alpha \gamma T$  is normally in the range of 0.01-0.02 for most ceramic solids.

The EoS most commonly used for fitting isothermal (i.e.  $P$ - $V$  datasets) are listed briefly below. Further details of the derivations and limitations can be found in, for example, Anderson (1995) and Angel (2000a).

**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:

$$V = V_0 \left( 1 + \frac{K'_0 P}{K_0} \right)^{-1/K'_0} \quad (1)$$

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 2000a) 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:

$$P = \frac{K_0}{K'_0} \left[ \left( \frac{V_0}{V} \right)^{K'_0} - 1 \right] \quad (2)$$

**Birch-Murnaghan.** This is a “Finite strain EoS”, and is based upon the assumption (e.g. Birch 1947) that the strain energy of a solid undergoing compression can be expressed as a Taylor series in the finite strain,  $f$ . There are a number of alternative definitions of  $f$ , each of which leads to a different relationship between  $P$  and  $V$ . The Birch-Murnaghan EoS (Birch 1947) is based upon the Eulerian strain,  $f_E = \left[ (V_0/V)^{2/3} - 1 \right] / 2$ . Expansion to fourth-order in the strain yields an EoS:

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

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):

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

**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:

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

This value for  $K''$  is normally substantially larger than that implied by the truncation of the 3rd-order Birch-Murnaghan EoS (Eqn. 4), and this may result in significantly different values of  $K_0$  being obtained from fits of the two equations to the same  $P$ - $V$  data, as in the worked example with quartz  $P$ - $V$  data, given below.

**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, 1987) 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, 1987) 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).

### ***Fitting Equations of State: EOSFIT.***

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 (2000a). Here the program EOSFIT, distributed with the course software, is used to illustrate the fitting of a  $P$ - $V$  dataset (Table 1).

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 EOSFIT program performs least-squares fit of  $P$ - $V$  data with pressure as the dependent variable. The dataset (see the quartzpv.dat file as an example) must be an ASCII file with one data point per line, delimited by commas. At minimum, each line must include a pressure and a volume. In



addition, each line may also include a value of esd(P) and/or a value for esd(V). If both are provided, esd(P) must be written before esd(V).

**Assignment of weights.** In any  $P$ - $V$  dataset, both the pressures and the volumes have experimental uncertainties associated with them. EOSFIT 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 EOSFIT 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 EOSFIT program (a summary of the results that you should obtain is given in Table 2):

Start the program in a DOS box from the directory in which the datafile (quartzpv.dat) is stored. The program first requests the name for a log file, and then the name of the data file:

INPUT NAME OF PRINT FILE: quartz.prt  
INPUT NAME OF DATA FILE: quartzpv.dat

The next display is the main menu, to which the program always returns after fitting an EoS:

SELECT ACTION:  
-1: EXIT  
0: SELECT NEW DATA FILE  
1: FIT EOS  
2: FIT LINEAR DATA  
ENTER SELECTION: 1

There now follow two menus that initialise the fitting of the EoS. At the first menu, select the Birch-Murnaghan P,V fit by entering “3”.

The next menu allows you to select the weighting scheme to be used in performing the least-squares process. It is normal to use weights derived from the uncertainties in both pressure and in volume, so select this option by entering “4”.

The least squares program requires some initial estimates of the values of the parameters to be refined, together with the values of those to be fixed in the refinement. For a second-order Birch-Murnaghan EoS the value of  $K'$  must be fixed at 4, the value implied by the truncation (see above). A reasonable guess for  $V_0$  is  $113\text{\AA}^3$ , and 45 GPa for  $K_0$  (these values are not critical). Therefore,

INPUT INITIAL VALUES OF PARAMETERS,  $V_0$ , K,  $K_p$ : 113,45,4.0

The program now calculates and prints the implied value for  $K_0''$  from your input parameters.

You now choose which parameters to refine at the next prompt: 1 for refine, 0 to fix. Thus, to refine a 2nd-order Birch-Murnaghan EoS:

INPUT 4 REFINEMENT FLAGS (1=YES, 0=NO): 1,1,0,0

The program performs the least-squares fit and terminates when the total sum of the parameter shifts divided by their esd's becomes insignificant. The parameter values after each least-squares cycle are printed to the log file. The parameter values after the last cycle are printed to the screen, together with their esd's (a summary is given in Table 2). Note also that the implied values for the unrefined parameters are also provided. The next pages (listed by entering a <CR>) list the observed and calculated values of the pressures, the difference  $P_{obs}-P_{calc}$ , and the weight of each data point. This is followed by a screen showing a number of fit parameters (all of this information is printed to the log

file). Note the large value of 128 for  $\chi_w^2$ , together with the maximum misfit,  $|P_{obs} - P_{calc}|_{max}$ , more than ten times larger than the esd in an individual data point 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:

FURTHER CALCULATIONS (Y/N)? y

which returns you to the main menu. Select EoS fit again by entering “1”, and proceed as above until the prompt to input the refinement flags. This time, refine the value of  $K'$  as well:

INPUT 4 REFINEMENT FLAGS (1=YES, 0=NO): 1,1,1,0

This expansion of the EoS to third-order reduces  $\chi_w^2$  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 menus again and refine a fourth-order Birch-Murnaghan EoS by setting all of the refinement flags to 1, so as to refine the value of  $K''$ . This yields only a marginal improvement in  $\chi_w^2$ , 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  $\chi_w^2$  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).

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

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P: GPa	a: Å	c: Å	V: Å <sup>3</sup>
10 <sup>-4</sup>	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)

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

	$V_0 : \text{\AA}^3$	$K_0 : \text{GPa}$	$K'$	$K'' : \text{GPa}^{-1}$	$\chi_w^2$	$ P_{obs} - P_{calc} _{\max}$ $\text{GPa}$
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.

### ***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  $a = a_0 + a_1P + a_2P^2$ , 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 program. The cubing of the lattice parameter and the transformation of its *esd* is performed by the program when the user selects the “Fit linear data” option. (The datafile format is the same as for  $P$ - $V$  data, except that the lattice parameter and its *esd* should be entered in the datafile). 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  $\beta_0$  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  $a\sin\beta$  against pressure with an EoS function, or the  $\beta$  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, 2000b). 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.

***Program release notes.***

The EOSFIT program is distributed on a non-commercial basis and the author would appreciate its use being acknowledged by reference to Angel (2000a) in any publications. I plan to re-write and expand the program with a GUI, incorporating a more flexible input-file format and the calculation of strain tensors. If you would like to receive program updates (including bug fixes), please register with me as a user by e-mail (ross.angel@uni-bayreuth). If you discover apparent bugs in the program, please send me both the input file, the output file and a full description of the problem by e-mail.

## REFERENCES

- Anderson OL (1995) Equations of state of solids for geophysics and ceramic science. Oxford University Press, Oxford.
- Angel RJ (1993) The high-pressure, high-temperature equation of state of calcium fluoride, CaF<sub>2</sub>. *J Phys: Cond Matter* 5:L141-L144
- Angel RJ (2000a) Equations of state. In Hazen RM (Ed), *Comparative Crystal Chemistry*. MSA Reviews in Mineralogy 39.
- Angel RJ (2000b) High-pressure structural phase transitions. In Redfern SAT (Ed), *Transformation Processes in Minerals*. MSA Reviews in Mineralogy 40.
- Angel RJ, Allan DR, Miletich R, Finger LW (1997) The use of quartz as an internal pressure standard in high-pressure crystallography. *J Appl Cryst* 30:461-466
- Angel RJ, Kunz M, Miletich R, Woodland AB, Koch M, Xirouchakis D (1999) High-pressure phase transition in CaTiOSiO<sub>4</sub> titanite. *Phase Transitions* 68:533-543
- Barnett JD, Block S, Piermarini GJ (1973) An optical fluorescence system for quantitative pressure measurement in the diamond-anvil cell. *Rev Sci Instrum* 44:1-9
- Besson JM, Nelmes RJ, Hamel G, Loveday JS, Weill G, Hull S (1992) Neutron diffraction above 10 GPa. *Physica B* 180 & 181:907-910
- Birch F (1947) Finite elastic strain of cubic crystals. *Phys Rev* 71:809-824
- Birch F (1986) Equation of state and thermodynamic parameters of NaCl to 300 kbar in the high-temperature domain. *J Geophys Res* 91:4949-4954
- Boffa-Ballaran T, Angel RJ, Carpenter MA (2000) High-pressure transformation behaviour of the cummingtonite-grunerite solid solution. *Euro J Miner*, accepted
- Brown, JM (1999) The NaCl pressure standard. *J Appl Phys* 86:5801-5808
- Chai M, Brown JM (1996) Effects of non-hydrostatic stress on the R lines of ruby single crystals. *Geophys Res Letts* 23:3539-3542
- Decker DL (1971) High-pressure equations of state for NaCl, KCl, and CsCl. *J Appl Phys* 42:3239-3244
- Decker DL, Petersen S, Debray D, Lambert M (1979) Pressure-induced ferroelastic phase transition in Pb<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>: A neutron diffraction study. *Phys Rev B* 19:3552-3555
- Eggert JH, Xu L-W, Che R-Z, Chen L-C, Wang J-F (1992) High-pressure refractive index measurements of 4:1 methanol: ethanol. *J Appl Phys* 72:2453-2461
- Gupta YM, Shen XA (1991) Potential use of the ruby R<sub>2</sub> line shift for static high-pressure calibration. *Appl Phys Letts* 58:583-585
- Hammersley AP, Svensson SO, Thompson A, Graafsma A, Kvick A, Moy JP (1995) Calibration and correction of distortions in 2D detector systems. *Rev Sci Instr* 66:2729-2733
- Hammersley AP, Svensson SO, Hanfland M, Fitch AN, Häusermann D (1996) Two-dimensional detector software: from real detector to idealised image or two-theta scan. *High Press Res* 14:235-248
- Hazen RM (2000) *Comparative Crystal Chemistry*. MSA Reviews in Mineralogy 39.
- Hazen RM, Finger LW (1981) Calcium fluoride as an internal pressure standard in high-pressure/high-temperature crystallography. *J Appl Crystallogr* 14:234-236



- Hazen RM, Finger LW (1989) High-pressure crystal chemistry of andradite and pyrope: revised procedures for high-pressure diffraction experiments. *Am Min* 74:352-359
- Heinz DL, Jeanloz R (1984) The equation of state of the gold calibration standard. *J Appl Phys* 55:885-893
- Holzappel WB (1997) Pressure determination. In: *High-Pressure Techniques in Chemistry and Physics* (WB Holzappel, NS Isaacs, eds) Oxford University Press, Oxford: pp 47-55
- Jeanloz R (1988) Universal equation of state. *Phys Rev B* 38:805-807
- Jessen SM, Küppers H (1991) The precision of thermal-expansion tensors of triclinic and monoclinic crystals. *J Appl Cryst* 24:239-242
- Klotz S, Besson JM, Hamel G, Nelmes RJ, Marshall WG, Loveday JS, Braden M (1998) *Rev High Pressure Sci Technol* 7:217-220
- Knorr K, Fütterer K, Annighöfer B, Depmeier W (1997) A heatable large volume high pressure cell for neutron powder diffraction: The Kiel-Berlin Cell I. *Rev Sci Instrum* 68:3817-3822
- Knorr K, Annighöfer B, Depmeier W (1999) A heatable large volume high pressure cell for neutron powder diffraction: The Kiel-Berlin Cell II. *Rev Sci Instrum* 70:1501-1504
- Kuhs W, Bauer FC, Hausmann R, Ahsbahs H, Dorwarth R, Hölzer K (1996) Single crystal diffraction with X-rays and neutrons: High quality at high pressure? *High Press Res* 14:341-352
- Miletich R, Allan DR, Kuhs WF (2000) High-pressure single-crystal techniques. In Hazen RM (Ed), *Comparative Crystal Chemistry*. MSA Reviews in Mineralogy 39.
- Murnaghan FD (1937) Finite deformations of an elastic solid. *Am J Math* 49:235-260
- Nomura M, Nishizaka T, Hirata Y, Nakagiri N, Fujiwara H (1982) Measurement of the resistance of Manganin under liquid pressure to 100 kbar and its application to the measurement of the transition pressures of Bi and Sn. *Jap J Appl Phys* 21:936-939
- Ohashi (1972) Program Strain. Program listing provided in Hazen and Finger (1982) *Comparative Crystal Chemistry*, John Wiley and Sons, New York.
- Orear J (1982) Least squares when both variables have uncertainties. *Am J Phys* 50:912-916
- Paufler PP, Weber T (1999) On the determination of linear thermal expansion coefficients of triclinic crystals using X-ray diffraction. *Euro J Min* 11:721-730
- Poirier J-P, Tarantola A (1998) A logarithmic equation of state. *Phys Earth Planet Int* 109:1-8
- Schlenker JL, Gibbs GV, Boisen MB (1975) Thermal expansion coefficients for monoclinic crystals: a phenomenological approach. *Am Min* 60:828-833
- Sharma SM, Gupta YM (1991) Theoretical analysis of R-line shifts of ruby subjected to different deformation conditions. *Phys Rev B* 43:879-893
- Sinogeikin SV, Bass JD (1999) Single-crystal elasticity of MgO at high pressure. *Phys Rev B* 59:R14141-R14144
- Thoms M, Bauchau S, Häusermann D, Kunz M, LeBihan T, Mezouar M, Strawbridge D (1998) An improved X-ray detector for use at synchrotrons. *Nucl Inst Meths Phys Res A* 413:175-184

- Vinet P, Ferrante J, Smith JR, Rose JH (1986) A universal equation of state for solids. *J Phys C: Solid State* 19:L467-L473
- Vinet P, Ferrante J, Rose JH, Smith JR (1987) Compressibility of solids. *J. Geophys Res* 92:9319-9325
- Vos WL, Schouten JA (1991) On the temperature correction to the ruby pressure scale. *J Appl Phys* 69:6744-6746