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On the creation of thermal equations of state for use in Dioptas

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ABSTRACT

Dioptas is a widely used software package for integrating and analysing 2-dimensional diffraction images. To help interpret the integrated diffraction profiles it produces, Dioptas users can input files that parameterise a material's thermal equation of state (EoS), enabling the positions of the Bragg peaks from that material to be calculated as a function of pressure and temperature. However, care is needed to ensure that these input files correctly describe the thermal EoS of interest. Here we describe the thermal EoS model used by Dioptas and show how existing thermal EoS should be reparameterised so as to be used correctly in Dioptas. Input EoS files suitable for use with Dioptas are provided for the following commonly-used pressure calibrants and pressure transmitting media: Al, Au, Cu, Mo, Nb, Pt, Ta, hcp-Fe, MgO, NaCl-B1, NaCl-B2, KCl-B2, and Ne.

1. Introduction

Since the early 1990s, the standard technique for collecting x-ray diffraction data from powdered samples at high pressure involves the collection of 2D Debye-Scherrer (D-S) diffraction images on area detectors, followed by azimuthal integration of the D-S rings to obtain standard 1D diffraction profiles [1–3]. Since the development of these angle-dispersive diffraction techniques, a number of different software packages with graphical interfaces have been written to perform the azimuthal integration of the 2D images [4–9]. Perhaps the most commonly used software package today to perform azimuthal integration is Dioptas [10], which is freely available and frequently updated.

One of the many useful features of Dioptas is that jcpds parameter files (named after the Joint Committee on Powder Diffraction Standards) for samples, pressure standards (*e.g.* Cu, Au), or pressure transmitting media (*e.g.* MgO, NaCl, KCl) can be read into the package and used to calculate the expected positions of diffraction peaks from those

materials as a function of pressure and temperature. This helps Dioptas users to identify all of the diffraction peaks present in their integrated diffraction profiles, and to make a quick estimate of the pressure in the sample chamber within seconds of the integrated profile appearing.

For diffraction data collected at 298 K, the jcpds input files need to contain values of V_0, K_0, and K' (the zero-pressure unit cell volume, the zero-pressure bulk modulus, and its pressure derivative), the zero-pressure lattice parameters, and a list of Miller indices, d-spacings, and intensities. Using these parameters, Dioptas calculates the unit cell parameters, and then the peak positions of the listed reflections, at a chosen pressure (P) and overlays them onto the integrated diffraction profile. The Dioptas user can then change the pressure with the click of a mouse, and see how the diffraction peaks change position as a function of P.

Fortuitously, the format of the jcpds files, developed at GSECARS/APS in the early 2000s by Mark Rivers, also allows the input of 4 additional parameters, $\alpha_{T=298\,K}$, $\partial\alpha_T/\partial T$, $\partial K_0/\partial T$ and $\partial K'/\partial T$ which are, respectively, the zero-pressure volumetric thermal expansion α_T at 298 K, and the linear temperature dependencies of α_T, K_0, and K'. From these four additional parameters, Dioptas constructs a thermal EoS from which the unit cell volume, and hence the positions of the Bragg peaks, can be predicted as a function of both P and temperature (T).

However, it has recently become clear to us that many who use the option of a thermal EoS in Dioptas do not understand what model of EoS the software uses, and therefore what are suitable values for the various input parameters. For example, a quick internet search for a suitable value for α_T for a material often returns the *linear* thermal expansion rather than the required *volumetric* value, resulting in a 3-fold underestimation of the thermal expansion and thus a 3-fold overestimation of the temperature required to obtain a specific unit cell volume at a given pressure. In this manuscript, we describe the form of the thermal EoS used in Dioptas and explain how least-squares fitting of either experimental or computed P-V-T EoS data in a spreadsheet can be used to obtain the optimised parameters for samples, pressure standards, and pressure transmitting media such that the EoS is accurately represented within the Dioptas framework. Finally, we provide a number of jcpds parameter files for materials that are widely used as high pressure high-temperature research, such as Au, Pt, Cu, MgO, NaCl, KCl and Fe, as well as parameter files for commonly used 'primary' pressure calibrants at room temperature (Mo, Cu, Au and Pt).

2. The Dioptas thermal EoS

The usual form of the calibrant parameter file read into Dioptas is a so-called jcpds file. An example of a Version 4 jcpds file is shown in Figure 1, and the format is described in Figure 2. Of key interest to this manuscript are the values of `VOLUME`, `K0`, `K0P`, `DK0DT`, `DK0PDT`, `ALPHAT` and `DALPHADT`, that is V_0, K_0, K', $\partial K_0/\partial T$, $\partial K'/\partial T$, α_T and $\partial\alpha_T/\partial T$.

The thermal EoS model used in Dioptas is the thermal pressure model of Anderson [12], in which the pressure at a given V and T is given by

$$P(V, T) = P(V, T_0) + \Delta P_{th}(T) \tag{1}$$

```
VERSION:     4
COMMENT: MgO, Fm-3m (Sokolova 2016: 0-100 GPa, 298-1500K)
K0:          161.10704
K0P:         4.0099769
DK0DT:       -0.006241
DK0PDT:      0.0001929
SYMMETRY: CUBIC
A:           4.2117329
B:           4.2117329
C:           4.2117329
ALPHA:       90.0
BETA:        90.0
GAMMA:       90.0
VOLUME:      74.70639
ALPHAT:      3.5023812e-05
DALPHADT:    7.7529586e-09
DIHKL:       2.43163    9.94117    1    1    1
DIHKL:       2.10585    100        2    0    0
DIHKL:       1.48906    64.4101    2    2    0
DIHKL:       1.26988    8.73692    3    1    1
DIHKL:       1.21581    20.3458    2    2    2
DIHKL:       1.05293    8.49446    4    0    0
DIHKL:       0.96623    3.06788    3    3    1
DIHKL:       0.941765   20.8962    4    2    0
DIHKL:       0.85971    13.8651    4    2    2
DIHKL:       0.810542   1.54772    5    1    1
```

Figure 1. Example of a Version 4 jcpds file. The 6 parameters used to establish the thermal EoS are `K0`, `K0P`, `DK0DT`, `DK0PDT`, `ALPHAT` and `DALPHADT`.

where T_0 is the reference temperature of 298 K, and $\Delta P_{th}(T)$ is the additional T-dependent thermal pressure relative to the 298 K isotherm given by

$$\Delta P_{th}(T) = \alpha_T(T)K_0(T)\Delta T \qquad (2)$$

where $\Delta T = (T - 298\ \text{K})$.

Importantly, Dioptas assumes a third order Birch-Murnaghan (B-M) EoS for the 298 K isotherm [13], and it is, therefore, essential that the values of V_0, K_0 and K' in the jcpds files should be those for this form of EoS, and not those obtained from fits to other forms of EoS, such as the Vinet [14] or AP2 [15,16]. While the parameters from these other EoSs can be very similar to those obtained by fitting the same data to a B-M EoS, this is not always the case, as will be shown later, and so refitting is typically required.

For temperatures other than 298 K, Dioptas calculates the thermal pressure correction that is applied to the 298 K EoS [12]. Dioptas does this by first calculating the values of

```
COMMENT:          Any information describing the material, literature
                  references, etc.  There can be multiple comment lines per
                  file.
K0:               The bulk modulus in GPa.
K0P:              The change in K0 with pressure, for Birch-Murnaghan
                  equation of state.  Dimensionless.
DK0DT:            The temperature derivative of K0, GPa/K.
DK0PDT:           The temperature derivative of K0P, 1/K.
SYMMETRY:         One of CUBIC, TETRAGONAL, HEXAGONAL, RHOMBOHEDRAL,
                  ORTHORHOMBIC, MONOCLINIC or TRICLINIC
A:                The unit cell dimension A
B:                The unit cell dimension B
C:                The unit cell dimension C
ALPHA:            The unit cell angle ALPHA
BETA:             The unit cell angle BETA
GAMMA:            The unit cell angle GAMMA
VOLUME:           The unit cell volume
ALPHAT:           The thermal expansion coefficient, 1/K
DALPHADT:         The temperature derivative of the thermal expansion
                  coefficient, 1/K^2
DIHKL:            For each reflection, the D spacing in Angstrom, the
                  relative intensity (0-100), and the H, K, L indices.
```

Figure 2. Descriptions of the input parameters of a Version 4 jcpds file [11].

$\alpha_T(T)$, $K_0(T)$ and $K'(T)$ at that value of T via

$$\alpha_T(T) = \alpha_{298} + \left.\frac{\partial \alpha_T}{\partial T}\right|_{298} \Delta T \tag{3}$$

$$K_0(T) = K_{0,298} + \left.\frac{\partial K_0}{\partial T}\right|_{298} \Delta T \tag{4}$$

$$K'(T) = K'_{298} + \left.\frac{\partial K'}{\partial T}\right|_{298} \Delta T \tag{5}$$

where $\Delta T = (T - 298\,\text{K})$, and α_{298}, $K_{0,298}$ and K'_{298} are the zero-pressure volumetric thermal expansion, the zero-pressure bulk modulus, and the change in $K_{0,298}$ with pressure, as determined at 298 K.

If the sample pressure is zero, then Dioptas calculates

$$V = V_0(1 + \alpha_T(T)\Delta T) = V_0\left(1 + \alpha_{298}\Delta T + \left.\frac{\partial \alpha_T}{\partial T}\right|_{298} \Delta T^2\right) \tag{6}$$

This is the volumetric expansion at $P=0$, and a comparison with experimental data provides a check of the correct values of α_{298} and $\partial \alpha_T/\partial T$. Indeed, as will be shown below, the values of α_{298} and $\partial \alpha_T/\partial T$ in the jcpds file can be obtained by fitting the volumetric thermal expansion at zero pressure.

If the sample pressure is greater than zero, then Dioptas calculates the associated cold curve pressure $P(V, T_0)$ using Equations (1) and (2)

$$P(V, T_0) = P(V, T) - \alpha_T(T)K_0(T)\Delta T \tag{7}$$

and then numerically solves the 3rd order B-M EoS to determine V/V_0 for the given values

of $K_0(T)$, $K'(T)$ and $P(V, T_0)$. We add a note of caution here that in cases where the second term of the right hand side of Equation (2) is greater than $P(V, T)$, the EoS framework in Dioptas returns negative values for $P(V, T_0)$. These negative pressures may then result in the calculated V/V_0 being >1 when the numerical solution to the B-M EoS is performed. In practice, this behaviour typically occurs at low sample pressures and high temperatures and can result in a non-physical volume expansion following small increases in the pressure above 0 GPa. Fortunately, the affected PT space is limited in extent and for most applications can be ignored. For example, in the case of MgO, at 1500 K, with $\alpha_T(T) = 4.434287 \times 10^{-5}$ K^{-1} and $K_0(T) = 153.6054$ GPa, the non-physical region is confined to < 1.05 GPa. This anomaly is illustrated in Figure 3(a) where the thermal expansion as calculated by Dioptas at $P = 0.01$ GPa is plotted alongside that calculated at $P = 0$ GPa. At temperatures above 600 K, the unit cell volume calculated at $P = 0.01$ GPa is clearly (and non-physically) *larger* than that calculated at 0 GPa at the same temperature.

We can see that of the 6 thermal EoS parameters in the jcpds file, two (K_0 and K') are obtained from a 3rd order B-M fit to the isothermal compression at $T_0 = 298$ K, two $\alpha_{T=298 K}$ and $\partial\alpha_T/\partial T$) are obtained from the zero pressure thermal expansion, and the final two ($\partial K_0/\partial T$, and $\partial K'/\partial T$) are obtained from P-V-T data with $P \neq 0$ GPa and $T \neq 298$ K. This provides a straightforward route to obtaining optimum values of these parameters:
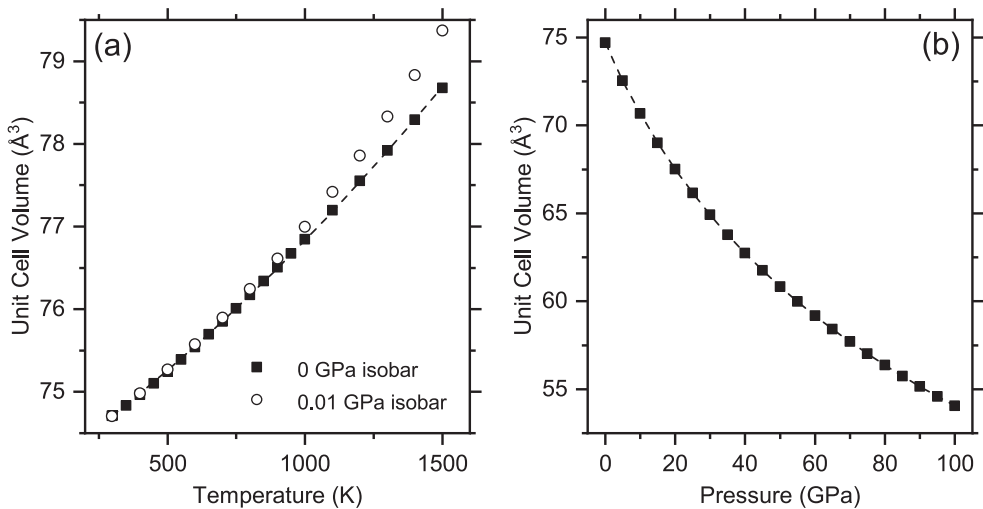
Figure 3. The solid data points show (a) the 0 GPa volumetric thermal expansion, and (b) the 298 K isothermal compressibility of MgO, as calculated from the Sokolova et al. thermal EoS [22]. The dashed line in (a) is the best fit to the thermal expansion using Equation (6), while the dashed line in (b) is the best fit to the compressibility using a 3rd order Birch-Murnaghan EoS. The unfilled data points in (a) show the thermal expansion of MgO at 0.01 GPa, as calculated by Dioptas using the jcpds input file shown in Figure 1. At a given temperature and this very low, but non-zero pressure, most of the MgO unit cell volumes calculated by Dioptas are greater than the associated volumes on the P=0 isobar, particularly at high temperatures. Effectively, Dioptas produces isotherms exhibiting expansion upon compression within a narrow pressure range. The reasons for this non-physical response are described in the main text.

(1) Fit the isothermal compression at 298 K with a 3rd order B-M EoS and thereby determine values for V_0, K_0 and K'. Fix these parameters.
(2) Fit the ambient pressure volumetric expansion data using Equation 6, and thereby determine values for α_T and $\partial\alpha_T/\partial T$. Fix these parameters.
(3) Using P_{obs}-V-T data with $P > 0$ GPa and $T \neq 298$ K, compute $P(V, T_0)$ and therefore $P_{calc}(V, T) = P(V, T_0) + \alpha_T(T)K_0(T)\Delta T$. Then compute $P_{obs} - P_{calc}$ for each P-V-T data point, and minimise the differences by optimising the values of $\partial K_0/\partial T$ and $\partial K'/\partial T$.

3. Obtaining Dioptas thermal EoS parameters

3.1. MgO

To illustrate how the jcpds file for an individual material can be determined we give the example of the thermal EoS of MgO, a material commonly used as a high-PT calibrant and pressure transmitting medium and on which there have been many previous studies of its thermal-EoS [17–22]. In obtaining optimum thermal EoS parameters for use in Dioptas we have chosen to reparameterise the existing thermal EoS of MgO recently published by Sokolova et al. which itself was optimised to fit a wealth of experimental data [22].

Sokolova et al. also used a thermal pressure model for their EoS, but used Holzapfel's Adopted Polynomial (AP2) EoS to describe the room temperature compression [16,23], and an Einstein model for the high-temperature behaviour [22]. This study was particularly useful in the current context as the authors provided Excel spreadsheets from which it was possible to straightforwardly calculate P or V at a given T for each material they studied despite the complexity of their thermodynamic model.

Firstly, we used Ref. [22] to calculate the unit cell volume at 20 pressures from ambient up to 100 GPa at 298 K, and the resulting compression curve is shown in Figure 3(b). Because Sokolova et al. used an AP2 EoS in their calculations, it is necessary to refit their compression data using a 3rd order B-M EoS rather than simply using their published AP2 values of K_0, K' (160.3 GPa and 4.10, respectively) directly. Otherwise, direct use of the parameters may result in a significant discrepancy between the Dioptas output and the true EoS behaviour. The best fit to the compression curve using a B-M EoS gave K_0=161.11 GPa and K'=4.010 and the resulting fit is shown in Figure 3(b).

Next, to obtain values for α_T and $\partial\alpha_T/\partial T$ we calculated the values of V at 21 different values of T from 298 to 1500 K at P=0.0001 GPa (atmospheric pressure) using Ref. [22]. The calculated volumes are shown in Figure 3(a), along with a fit using Equation (6). From this fit, the best fitting values of α_T and $\partial\alpha_T/\partial T$ are 3.502×10^{-5} K^{-1} and 7.753×10^{-9} K^{-2}, respectively.

Finally, in order to determine the optimum values of $\partial K_0/\partial T$ and $\partial K'/\partial T$, we used Ref. [22] to calculate P over a grid of 234 V-T values spanning 18 volumes from 74 to 53.6 Å^3 (which equates to a pressure range of approximately 0–100 GPa – see Figure 3(b)) and 15 temperatures from 298 to 1500 K. Using the Solver minimisation routine in Excel, we then optimised the values of $\partial K_0/\partial T$ and $\partial K'/\partial T$ while fixing the values of the other 4 parameters. The best fitting values were -0.006241 GPa K^{-1} and 0.000193 K^{-1}, respectively. The final jcpds file is shown in Figure 1.

The differences in calculated pressures, over a range of volumes and temperatures to ~100 GPa and 1500 K, between the Sokolova thermal EoS and the best-fitting Dioptas EoS is shown in Figure 4. The maximum differences, of ~0.8 GPa, are seen at low pressures
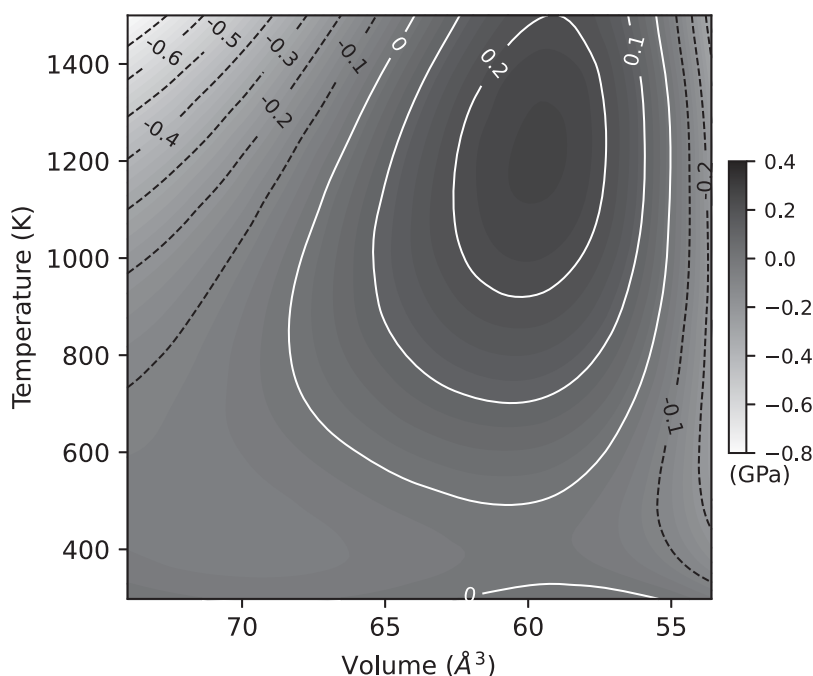
Figure 4. The differences in pressures calculated by the Sokolova et al. thermal EoS for MgO as a function of the unit cell volume and temperature, and the reparameterisation suitable for use in Dioptas via import of a jcpds file. The shown volume scale equates to a pressure range of approximately 0–100 GPa.

and high temperatures. The agreement between the Sokolova EoS and its reparameterisation for use in Dioptas is further illustrated in Figure 5 which shows three *P-V* isotherms at 298, 1000 and 1500 K, as calculated by the Sokolova EoS, and the Dioptas-calculated pressures at a number of different volumes at the same three temperatures. The agreement is excellent.

If the thermal EoS within Dioptas is required to cover a different, or larger, *P-T* range to that used here then it is straightforward to refit and optimise the parameters over different or more extended ranges of *P-V-T* data.

3.2. Neon

Ne is a commonly used pressure transmitting medium, and its compressibility and thermal EoS have therefore been the subject of several previous studies [24–26]. In Ne, the values of V_0, K_0 and K' can again be obtained by fitting the room temperature isotherm with a 3rd order B-M EoS. Although solid Ne is only obtained above 4.7 GPa at 298 K [24] a value for V_0 can still be obtained from the B-M fit.

The fact that Ne is a gas at ambient conditions also means that the thermal expansion of solid-Ne is unknown above 298 K at atmospheric pressure and so the method described in the previous section for determining the values of α_T and $\partial\alpha_T/\partial T$ cannot be used in this case. However, values for α_T and $\partial\alpha_T/\partial T$ can be obtained simultaneously with the values of $\partial K_0/\partial T$ and $\partial K'/\partial T$, by allowing all 4 parameters to vary when minimising the differences between the calculated pressures over a grid of *V-T* data.
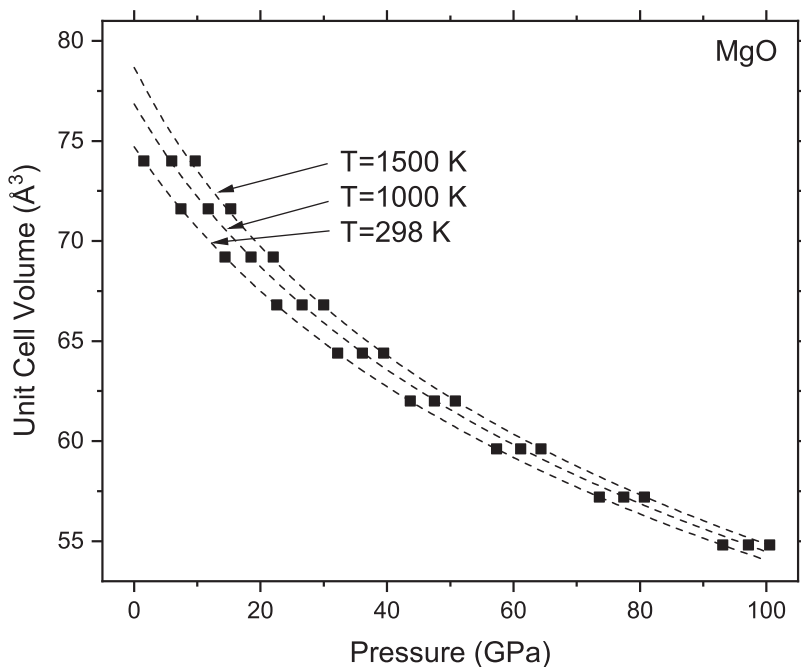
Figure 5. The 298, 1000 and 1500 K isotherms for MgO represented by the black dashed lines, as calculated using the thermal EoS of Sokolova et al. [22]. The black square data points show a number of *P-V* data points along the three isotherms, as calculated by Dioptas using the jcpds file shown in Figure 1.

In obtaining a suitable Ne jcpds input file for Dioptas we have chosen to reparameterise the thermal EoS of Ne published previously by Fei et al. [25]. This used a thermal pressure model with both a Vinet and B-M 298 K isotherm, and a Mie–Grüneisen thermal pressure. Using this EoS we first calculated the 298 K compressibility and fitted it with a B-M EoS. As expected, we obtained values of $V_0 = 88.967$ Å^3/cell, $K_0 = 1.16$ GPa and $K' = 8.23$, exactly the same as those reported in Fei et al.'s 298 K B-M EoS [25].

We then used the thermal EoS of Fei et al. to calculate the pressure at 144 $V - T$ points covering a range of 54 to 24 Å^3, equivalent to a pressure range of 5–150 GPa, and 400 to 2000 K, and varied α_T, $\partial\alpha_T/\partial T$, $\partial K_0/\partial T$ and $\partial K'/\partial T$ simultaneously to minimise the difference between the Fei EoS and the Dioptas EoS. The optimised EoS parameters are given in Table 1, and the agreement between the two EoSs is illustrated in Figure 6 which shows the isotherms at 298, 1000 and 2000 K, as calculated by the Fei EoS, and the calculated volumes at a number of points along the 1000 and 2000 K isotherms, as calculated by Dioptas. The agreement is excellent.

3.3. hcp-Fe

The hcp phase of Fe (ε-Fe) is stable from 14 GPa up to at least 300 GPa at 298 K [28]. While early studies suggested the existence of further high-temperature, high pressure phases, the most recent laser-heating studies of hcp-Fe suggest it is the only stable phase up to 377 GPa and 5700 K, conditions corresponding to Earth's inner core [29].

Table 1. The optimised thermal EoS parameters required for the jcpds files of various materials. V_0 is the unit cell volume for each material at ambient pressure, while the meanings of the other parameters are described in the main text.

Material	V_0 (Å^3/cell)	K_0 (GPa)	K'	α (10^{-5} K^{-1})	$\partial\alpha_T/\partial T$ (10^{-8} K^{-2})	$\partial K/\partial T$ (GPa K^{-1})	$\partial K'/\partial T$ (K^{-1})
MgO [22]	74.711★	161.107	4.010	3.502	0.775	−0.00624	0.000193
Al [22]	66.288★	76.174	4.136	6.527	4.395	−0.00914	0.000332
Au [22]	67.849★	169.669	5.662	3.911	1.403	−0.01017	0.000330
Cu [22]	47.239★	137.606	4.952	4.744	1.735	−0.01078	0.000412
Mo [22]	31.115★	261.274	4.122	1.359	0.491	−0.00945	0.000139
Nb [22]	35.961★	169.297	3.711	2.040	0.358	−0.00372	0.000069
Pt [22]	60.384★	277.936	5.158	2.572	0.578	−0.01312	0.000303
Ta [22]	36.070★	191.797	3.756	1.942	0.206	−0.00388	0.000077
NaCl (B1) [20]	179.113	25.079	4.569	11.927	7.132	−0.00529	0.001114
NaCl (B2) [25]	41.350	30.690	4.330	10.719	−0.893	0.00096	−0.000047
KCl (B2) [31]	52.953	24.606	4.540	8.944	0.173	−0.00028	0.000036
hcp-Fe [27]	22.642	150.475	5.537	5.051	−0.280	0.00713	−0.000174
Ne [25]	88.967	1.430	8.020	310.340	−7.539	0.00011	−0.000279
Cu [35]	47.219	136.922	4.921	0	0	0	0
Au [36]	67.716	178.548	5.327	0	0	0	0
Pt [36]	60.408	267.319	5.395	0	0	0	0
Mo [34]	31.095	260.607	3.965	0	0	0	0
Ta [37]	36.093	168.015	4.140	1.145	0.675	−0.00079	0.000007

Notes: V_0 values denoted ★ were held fixed during the refinement at the values given in [22].
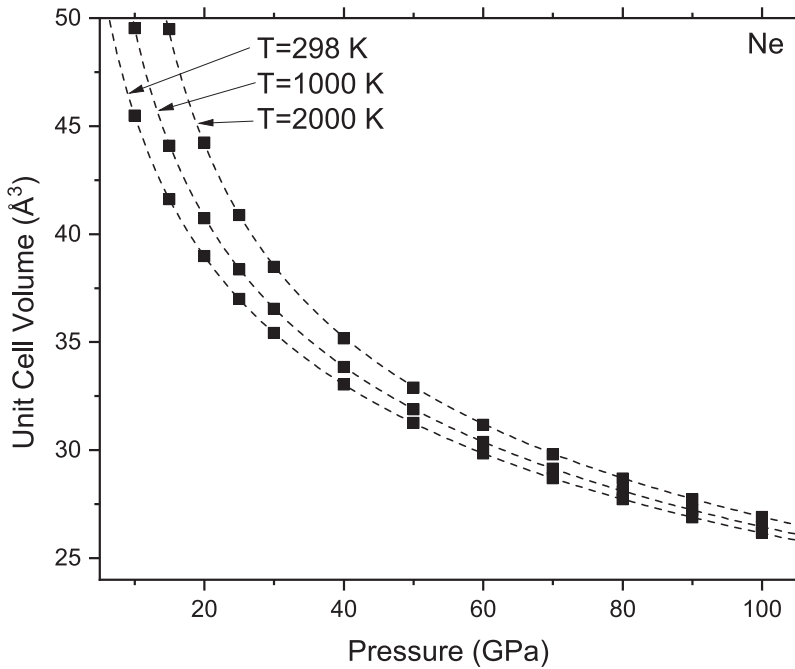

Figure 6. The 298, 1000 and 2000 K isotherms for Ne, as calculated using the thermal EoS of Fei et al. [25] are shown by the black dashed lines. The filled squares show a number of P-V data points along the 1000 and 2000 K isotherms, as calculated by Dioptas using the jcpds file input parameters for Ne given in Table 1.

In determining a Dioptas-suitable thermal EoS for hcp-Fe, we have chosen to reparame-terise the recent EoS by Dorogokupets et al. [27], which, as with results of Sokolova et al. [22], was provided with spreadsheets so as to simplify the complex P-V-T calculations.

In hcp-Fe, the values of V_0, K_0 and K' were again obtained by fitting the room temp-erature isotherm with a 3rd order B-M EoS. Fitting P-V data at 5 GPa intervals between atmospheric pressure and 100 GPa, as calculated using the EoS of Dorogokupets et al. [27], gave best fitting parameters of 22.642 Å^3/atom (fixed), 150.475 GPa and 5.537, respectively.

Similar to the case of Ne, it is not possible to determine α_T and $\partial\alpha_T/\partial T$ for hcp-Fe from the ambient pressure thermal expansion as this phase is stable only at high pressures. As with Ne therefore, values for α_T and $\partial\alpha_T/\partial T$ were obtained simultaneously with the values of $\partial K_0/\partial T$ and $\partial K'/\partial T$, by allowing all 4 parameters to vary when minimising the differ-ences between the calculated pressures over a grid of V-T data.

We used the Dorogokupets et al. thermal EoS to calculate the pressure at 63 V-T points over a volume range of 17 to 21 Å^3, equivalent to a pressure range of 15–120 GPa, and over a temperature range of 500 to 3000 K, and varied α_T, $\partial\alpha_T/\partial T$, $\partial K_0/\partial T$ and $\partial K'/\partial T$ simultaneously to minimise the difference between the pressures calculated by the Dorogokupets EoS and the Dioptas EoS. The optimised values for the jcpds input parameters are given in Table 1, and the agreement between the two equations of state is illustrated in Figure 7 which shows the isotherms at 298, 1000, 2000 and 3000 K, as calculated by the Dorogokupets EoS, and the calculated volumes at a number of points along the 1000, 2000, and 3000 K isotherms as calculated by Dioptas. The agree-ment is excellent.

Note that in calculating the positions of the diffraction peaks from hcp-Fe it is necess-ary to know the c/a ratio of the hexagonal structure. For hcp-Fe c/a is slightly pressure dependent [30], something that the jcpds file format is unable to account for. In preparing a jcpds file for hcp-Fe, we have therefore fixed the c/a ratio at 1.6 [30], and hence $a = 2.5376$ Å and $c = 4.0601$ Å at ambient pressure.

3.4. B2-KCl

KCl is often used as a pressure transmitting medium in high pressure laser heating exper-iments as it is soft, chemically inert, transparent in the near-infrared, and has a high melting temperature. At ambient conditions, KCl has the NaCl (B1) structure but trans-forms to the CsCl (B2) structure at ~2 GPa, which is stable to 165 GPa at room temperature and also at high temperatures. Establishing a thermal EoS for KCl enables it to be used as a pressure calibrant at high pressures and temperatures. There have been two recent papers establishing a thermal EoS for KCl, by Dewaele et al. [31] and Chidester et al. [32]. Since the Dewaele EoS has been used by others in laser heating experiments we have chosen to parameterise that EoS here.

Dewaele et al. again used a thermal pressure model to fit their data, where the thermal pressure term $P_{th}(V, T)$ could be approximated by $\overline{\alpha K_T}\Delta T$, where $\overline{\alpha K_T}$ is a constant. Hence:

$$P(V, T) = P(V, 300\text{K}) + \overline{\alpha K_T} \times (T - 300\text{K}) \tag{8}$$
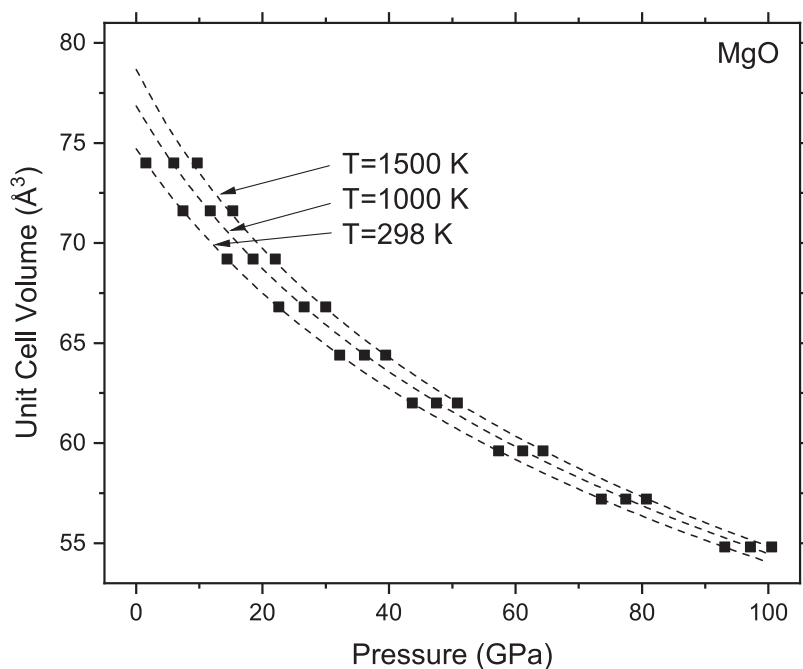
where $\overline{\alpha K_T} = 0.00244$ GPa K^{-1} [31].

Figure 7. The 298, 1000, 2000 and 3000 K isotherms for hcp-Fe (ε-Fe), as calculated using the thermal EoS of Dorogokupets et al. [27]. The filled squares show a number of *P-V* data points along the 1000, 2000 and 3000 K isotherms, as calculated by using the jcpds file input parameters for hcp-Fe given in Table 1.

In order to make a thermal EoS for B2-KCl suitable for use in Dioptas, we first calculated the 300 K compressibility using the Vinet EoS used by Dewaele et al. and then refitted it with a 3rd-order B-M EoS, giving optimised V_0, K_0 and K' values of 52.953 Å^3, 24.606 GPa and 4.540, respectively. Note that rather than fixing the value of V_0 at 54.5 Å^3, the value reported by Dewaele et al., we optimised V_0 simultaneously with those of K_0 and K' in order to improve the fit of the B-M EoS to the calculated compressibility at 300 K, which was otherwise poor.

We then used the thermal pressure model employed by Dewaele et al. to calculate the pressure at 112 *V-T* points over a volume range of 50 to 24 Å^3, equivalent to a pressure range of 2–130 GPa, and a temperature range of 500 to 3000 K. We then varied α_T, $\partial\alpha_T/\partial T$, $\partial K_0/\partial T$ and $\partial K'/\partial T$ simultaneously to minimise the difference between the pressures calculated by the Dewawele EoS and the Dioptas EoS.

Unsurprisingly, given the thermal EoS model used by Dewaele, the optimised values of $\partial\alpha_T/\partial T$, $\partial K_0/\partial T$ and $\partial K'/\partial T$ were all close to 0, while the optimised value of α_T was $8.944\times10^{-5}\ K^{-1}$.

The optimised values for the parameters are given in Table 1, and the agreement between the two equations of state is illustrated in Figure 8 which shows the isotherms at 300, 2000 and 3000 K, as calculated from the thermal EoS parameters given by Dewaele et al., and the calculated volumes at a number of points along the same three isotherms as calculated by Dioptas. The agreement is, once again, excellent.
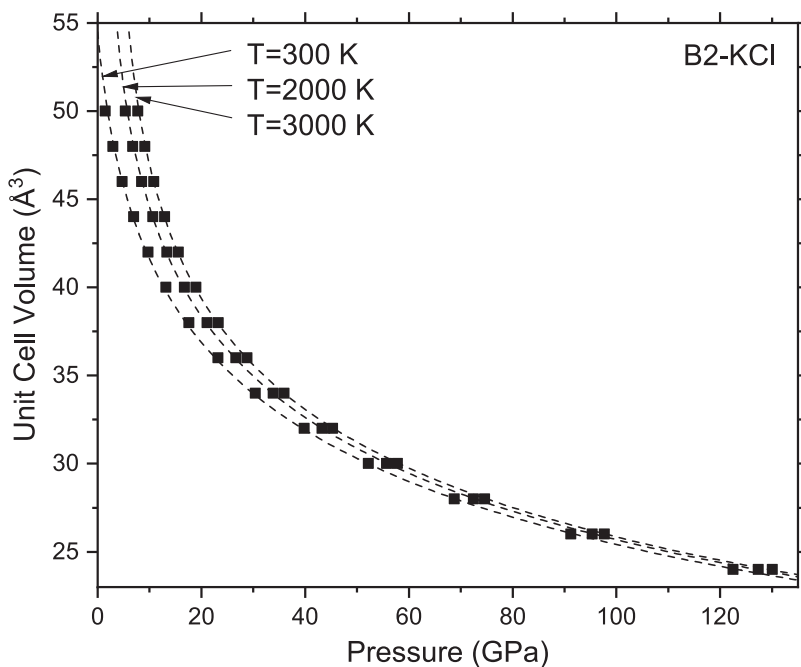
Figure 8. The 300, 2000 and 3000 K isotherms for the B2 phase of KCl, as calculated using the thermal EoS of Dewaele et al. [31]. The filled squares show a number of data points along the same isotherms, as calculated by using the jcpds file input parameters for B2-KCl given in Table 1.

3.5. Other common standards

We have repeated the analysis described above for a number of other materials whose thermal-EoS were parameterised by Sokolova et al. [22], along with that of both the B1 and B2 phases of NaCl [20,25]. The resulting best-fitting parameters are given in Table 1, and the resulting jcpds files are provided in the Supplementary Material. We stress again that in all cases we are *not* developing new thermal EoSs for these materials but rather reparameterising *existing* thermal EoSs so that they are suitable for use with Dioptas after importing them via jcpds files.

Note that for NaCl-B1 we first attempted to reparameterise the thermal EoS of Dorogokuopets and Dewaele [20], obtaining values of α_T, $\partial\alpha_T/\partial T$, $\partial K_0/\partial T$ and $\partial K'/\partial T$ simultaneously by fitting the isochore data given in Table 10 of Ref. [20]. Unfortunately, the resulting values of α_T and $\partial\alpha_T/\partial T$ did not give a good fit to the known ambient pressure thermal expansion [33]. Fortunately, the authors of Ref. [20] were able to provide us with a greater number of P-V-T data points using their EoS, including the ambient pressure thermal expansion of NaCl. α_T and $\partial\alpha_T/\partial T$ could then be determined independently of $\partial K_0/\partial T$ and $\partial K'/\partial T$, with the resulting values giving a good fit to the thermal expansion at ambient pressure.

3.6. Room temperature 'Primary' pressure standards to 300 GPa

To help Dioptas users obtain accurate pressures in samples compressed to high pressures at room temperature, we provide jcpds input files for the room temperature EoS of 4

'primary' pressure standards – Mo, Cu, Au and Pt – to 300 GPa. The first two of these were considered by an AIRAPT working group to establish an International Practical Pressure Scale [34], while Au and Pt have recently been proposed as pressure calibrants at TPa pressures [35,36]. In each case we have taken the published room temperature equations of state for Mo (AP2 [34]), Cu (3rd order Vinet [35]), Au and Pt (2nd order Vinet [36]), calculated their compression curves up to ~300 GPa, and then refitted these using a B-M EoS. The resulting fits are illustrated in Figure 9 and the best fitting parameters are given in Table 1.

In reparameterising these pressure standards, it is informative to compare the parameters originally published for the AP2 and Vinet equations of state for Mo, Au and Pt, with those obtained from the B-M fits. These are shown in Table 2, and highlight
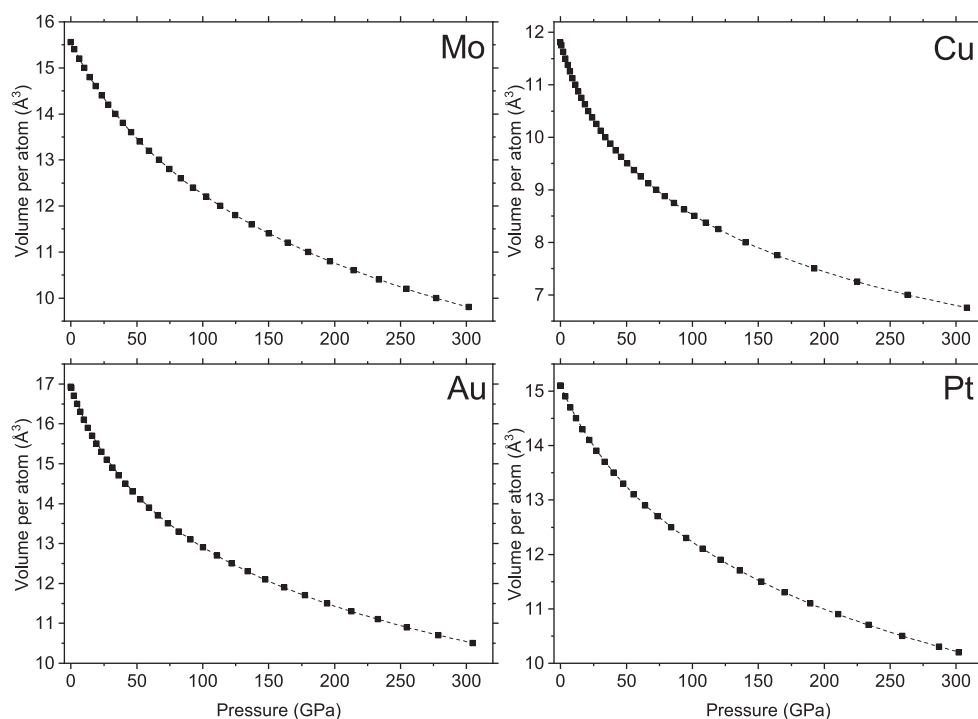

Figure 9. The room temperature equations of state of Mo, Cu, Au and Pt to 300 GPa. The data points show the calculated compressions using published AP2 (Mo) [34], 3rd order Vinet (Cu) [35], and 2nd order Vinet (Au and Pt) equations of state [36]. The dashed lines through the data points are the best-fitting B-M equations of state, using the parameters listed in Table 1.

Table 2. The as-published parameters for the room temperature AP2 EoS of Mo [34], and the Vinet EoS of Au and Pt [36].

Metal	V_0 (fixed) (Å³/atom)	EoS	K_0 (GPa)	K'	EoS	K_0 (GPa)	K'
Mo	15.547	AP2	260 (fixed)	4.00(1)	B-M	260.607	3.965
Au	16.929	Vinet	170.90(24)	5.880(5)	B-M	178.548	5.327
Pt	15.102	Vinet	259.70(16)	5.839(3)	B-M	267.319	5.395

Notes: V_0 is the atomic volume at ambient pressure. For comparison, the values of K_0 and K' obtained by refitting these equations of state with a Birch-Murnaghan (B-M) EoS are also shown.

the very different values for K_0 and K' required by the different EoS to produce almost identical compression curves (see Figure 9). This emphasises the importance of using the appropriate B-M values for V_0, K_0 and K' when using an existing EoS in Dioptas, rather than using the values obtained from fitting a different form of EoS. Interestingly, the parameters for the AP2/B-M fits for Mo in Table 2 are much more similar than those obtained for the Vinet/B-M fits to Au and Pt, where the differences in the values of K_0 and K' in the two EoS are 30–150 times larger than the uncertainties obtained in the Vinet fits.

3.7. Tantalum thermal EoS to 2.3 TPa and 5000 K

Finally, we have reparametarised the very recently published thermal EoS of Ta, as determined to 2.3 TPa and 5000 K using a combination of ramp and shock compression data [37]. This study greatly extends previous studies of the thermal EoS of tantalum, and, as the authors suggest, enables Ta to be used as a pressure calibrant in laser-heated static compression experiments which have recently been able to reach TPa pressures and thousands of degrees Kelvin. Reparameterising the published EoS was straightforward and followed the process described above. The values of α_T and $\partial\alpha_T/\partial T$ were obtained by fitting the known ambient pressure thermal expansion, while the values of K_0 and K' were obtained by calculating the isothermal compression at 298 K to 2300 GPa using the 3rd order Vinet EoS employed by Gorman et al. [37], and then refitting with a 2nd order B-M EoS. The 5 isotherms parameterised by Gorman et al. were then used to calculate a grid of 154 P-V points covering 0–2300 GPa and 298–5000 K from which the optimised values of $\partial K_0/\partial T$ and $\partial K'/\partial T$ were obtained. The best fitting parameters are given in Table 1 and the resulting jcpds file is provided in the Supplementary Material. The agreement between the Gorman and Dioptas equations of state is illustrated in Figure 10 which shows the difference in pressures as calculated from the thermal EoS parameters given by Gorman et al. [37], and those calculated by Dioptas using the parameters in Table 1. The agreement is, once again, excellent. Indeed over the full 0–2300 GPa, 298–5000 K range, the maximum difference between the pressures calculated by two equations of state was only 8 GPa.

4. Limitations

While the results in the previous section show that the thermal pressure model within Dioptas is capable of reproducing the isotherms calculated by other thermal EoSs with a high degree of accuracy, there are a number of limitations. The jcpds files assume the Birch-Murnaghan formalism to describe the isothermal compression at 298 K. This is known to give a poorer fit to experimental data than other formalisms such as Vinet [14] or AP2 [16,23], particularly at higher compressions, and it has been recommended that the BM EoS not be extrapolated beyond the data range to which it is fitted [15].

Secondly, there may be no high-temperature thermal expansion data at 0 GPa from which to determine α_T and $\partial\alpha_T/\partial T$ (as in the cases of Ne, hcp-Fe and B2-KCl above). However, as we have shown, these parameters can be optimsed from the high PT data simultaneously with $\partial K_0/\partial T$ and $\partial K'/\partial T$. In such cases, the values of α_T and $\partial\alpha_T/\partial T$ have no physical meaning.
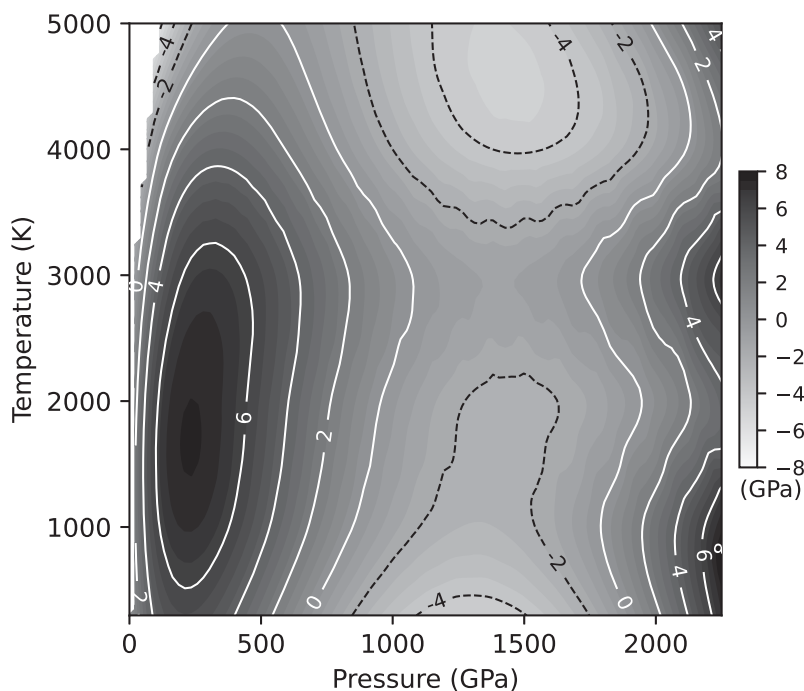
Figure 10. The differences in pressures between those calculated by the Gorman et al. thermal EoS for Ta, and those calculated by Dioptas using the parameters given in Table 1. Despite the very large *P-T* range (2300 GPa and 5000 K) the maximum difference between the two equations of state is only ~8 GPa at 240 GPa and 1750 K. No countours are shown in the white area at low pressures (<100 GPa) and high temperatures (3300–5000 K) as Ta is in the liquid state at such conditions.

Because of such limitations, we emphasise the importance of using the original EoS published in the literature for performing any final, in-depth analysis of new experimental data rather than the models and parameters presented here. The parameters given in Table 1 are intended to enable the Dioptas user to closely reproduce the behaviour of published EoS models within Dioptas for the purposes of performing rapid analysis in real-time of experimental data collected on synchrotrons and x-ray free electron lasers. The insight gained from such feedback would facilitate users to make well-informed decisions during such experiments.

5. Conclusions

One of the advantages of Dioptas over other azimuthal integration software packages is its ability to read in jcpds files, and hence equation of states, for pressure calibration purposes. The jcpds file format allows thermal equations of state to be imported, but care must be taken to ensure that these are parameterised correctly. We have demonstrated how this can be achieved by reparameterising a number of existing equations of state, for a range of different materials, in the correct format for use in Dioptas. We have provided the required parameters in tabulated form, as well as the relevant jcpds files, and the spreadsheets used to obtain the parameters for each material. The jcpds files are

also available for download with the most recent version of Dioptas available from https://github.com/Dioptas/Dioptas/releases.

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Disclosure statement

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