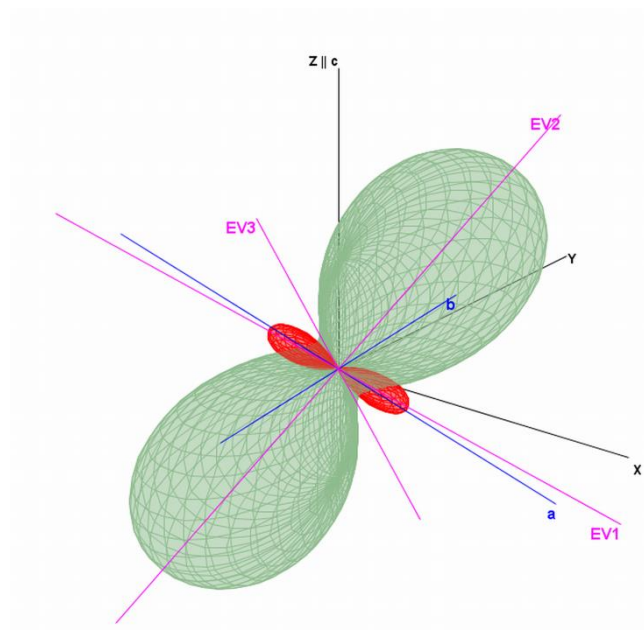


TEV

V1.0.1

A program for the determination and visualization of the thermal expansion tensor from diffraction data



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General information and prerequisites for working with TEV

TEV (Thermal Expansion Visualizing) is a user-friendly program for the calculation of the thermal expansion tensor α_{ij} from diffraction data. Unit cell parameters determined from temperature dependent data collections can be provided as input. An intuitive graphical user interface enables fitting of the evolution of individual lattice parameters to polynomials up to fifth order. Alternatively, polynomial representations obtained from other fitting programs or from the literature can be entered. The polynomials and their derivatives are employed for the calculation of the tensor components of α_{ij} in the infinitesimal limit following the approach described by Paufler & Weber (1999). The tensor components, eigenvalues, eigenvectors as well as their angles with the crystallographic axes can be evaluated for individual temperatures or for specific temperature ranges. Values of the tensor in specific directions parallel to either [uvw]'s of the crystal lattice or vectors (hkl) of reciprocal space can be calculated. Finally, the 3-D representation surface for the second rank tensor and pre- or user-defined 2-D sections can be plotted and saved in a bitmap (PNG) format.

TEV is written in JAVA. The program uses several libraries that are listed under the menu point "Help". A prerequisite for working with TEV is the installation of the JAVA runtime environment version 7 which can be downloaded from the following link: <http://www.java.com/en/download/>. The distribution contains an EXE-file for Windows users and a system independent JAR-file for running the software under Linux and Mac OS X. Furthermore, three test files containing temperature dependent data sets from hexagonal, monoclinic and triclinic compounds, a short manual (this document) and several license files for the libraries are included.

Mathematical background

A second rank tensor (such as the tensor of thermal expansion α_{ij}) is usually referred to an orthogonalized coordinate system $\{\mathbf{e}_1, \mathbf{e}_2, \mathbf{e}_3\}$. In general, there is an infinite number of ways how this reference system could be selected. In TEV, this system was chosen in such a way that it can be derived from the crystallographic basis vectors $\{\mathbf{a}, \mathbf{b}, \mathbf{c}\}$ according to the following relations: \mathbf{e}_3 is parallel to \mathbf{c} , \mathbf{e}_2 is parallel to \mathbf{b}^* and $\mathbf{e}_1 = \mathbf{e}_2 \times \mathbf{e}_3$ (in order to create a right-handed coordinate system). In more detail, these relationships can be expressed as follows:

$$\begin{pmatrix} \mathbf{a} \\ \mathbf{b} \\ \mathbf{c} \end{pmatrix} = \begin{pmatrix} a \sin(\beta) & 0 & a \cos(\beta) \\ -b \sin(\alpha) \cos(\gamma^*) & b \sin(\alpha) \sin(\gamma^*) & b \cos(\alpha) \\ 0 & 0 & c \end{pmatrix} \cdot \begin{pmatrix} \mathbf{e}_1 \\ \mathbf{e}_2 \\ \mathbf{e}_3 \end{pmatrix}$$

Notably, this selection guarantees that for the first (second) setting of the monoclinic crystal system the symmetry defining directions **c** (**b**) are parallel to **e**₃ (**e**₂), respectively.

One possible way to determine the tensor of thermal expansion α_{ij} of a crystalline material stems from the evaluation of the temperature dependence of the unit cell parameters $a, b, c, \alpha, \beta, \gamma$, which can be obtained from diffraction experiments. In the literature, several procedures have been described how this goal can be accomplished (Schlenker *et al.*, 1975; Schlenker *et al.*, 1978; Haussühl, 1983; Jessen & Küppers, 1991; Paufler & Weber, 1999). A discussion of the pros and cons of the different methods can be found in the paper of Paufler & Weber. TEV is based on the formalism that was presented by the latter authors, where the temperature increments are treated in the infinitesimal limit. This approach is of special value for the monoclinic and triclinic crystal systems where the orientation of the principal axes of the thermal expansion tensor can either partially or completely change as function of temperature.

In the first step of the calculations, the temperature evolution of the relevant lattice parameters must be described by a continuous function of T. In the present version of TEV, polynomials up to fifth order can be used for this purpose. The temperature dependency of a for a third order polynomial can be parameterized as:

$$a(T) = p_0 + p_1 \cdot T + p_2 \cdot T^2 + p_3 \cdot T^3$$

Numerically, the quality of the fitting can be described by the coefficient of determination R^2 :

$$R^2 = \frac{\sum_{i=1}^n (a_i - \bar{a})^2 - \sum_{i=1}^n (a_i - \hat{a}_i)^2}{\sum_{i=1}^n (a_i - \bar{a})^2}$$

(a_i : observed value no. i, \hat{a}_i : calculated value no. i, \bar{a} : mean, n : no. of different temperatures)

In the second step, the six independent α_{ij} components (for the most general triclinic case) can be related to the lattice parameters and their derivatives according to the following mathematical expressions:

$$\alpha_{11} \approx \frac{1}{a} \frac{da}{dT} + \frac{d\beta}{dT} \cot(\beta)$$

$$\alpha_{22} \approx \frac{1}{b} \frac{db}{dT} + \frac{d\alpha}{dT} \cot(\alpha) + \frac{d\gamma^*}{dT} \cot(\gamma^*)$$

$$\alpha_{33} \approx \frac{1}{c} \frac{dc}{dT}$$

$$\alpha_{12} \approx \frac{1}{2} \cot(\gamma^*) \left(\frac{1}{a} \frac{da}{dT} - \frac{1}{b} \frac{db}{dT} - \frac{d\alpha}{dT} \cot(\alpha) + \frac{d\beta}{dT} \cot(\beta) \right) + \frac{1}{2} \frac{d\gamma^*}{dT}$$

$$\alpha_{13} \approx \frac{1}{2} \left(\frac{1}{a} \frac{da}{dT} - \frac{1}{c} \frac{dc}{dT} \right) \cot(\beta) - \frac{1}{2} \frac{d\beta}{dT}$$

$$\alpha_{23} \approx \frac{1}{2} \left(\left(\frac{1}{a} \frac{da}{dT} - \frac{1}{c} \frac{dc}{dT} \right) \cot(\gamma^*) \cot(\beta) + \left(\frac{1}{b} \frac{db}{dT} - \frac{1}{c} \frac{dc}{dT} \right) \frac{\cot(\alpha)}{\sin(\gamma^*)} - \left(\frac{1}{\sin(\gamma^*)} \frac{d\alpha}{dT} + \frac{d\beta}{dT} \cot(\gamma^*) \right) \right)$$

The relationships for the other crystal systems follow directly from simplifications of these equations according to restrictions in and/or dependencies between the values of the parameters a , b , c , α , β and γ .

Using the components of the symmetrical α_{ij} -tensor, the value of the thermal expansion can be calculated for any direction which can be defined by a vector \mathbf{q} whose three components are the direction cosines q_1 , q_2 and q_3 , i.e. the cosines of the angles between the vector \mathbf{q} and the three axes of the orthogonalized reference system $\{\mathbf{e}_1, \mathbf{e}_2, \mathbf{e}_3\}$:

$$\alpha^{q_1, q_2, q_3} = (q_1 \quad q_2 \quad q_3) \cdot \begin{pmatrix} \alpha_{11} & \alpha_{12} & \alpha_{13} \\ \alpha_{12} & \alpha_{22} & \alpha_{23} \\ \alpha_{13} & \alpha_{23} & \alpha_{33} \end{pmatrix} \cdot \begin{pmatrix} q_1 \\ q_2 \\ q_3 \end{pmatrix}$$

Frequently, the values of α_{ij} in directions parallel to a crystallographic direction $\mathbf{t} = u \mathbf{a} + v \mathbf{b} + w \mathbf{c}$ or parallel to a reciprocal lattice vector $\mathbf{r}^* = h \mathbf{a}^* + k \mathbf{b}^* + l \mathbf{c}^*$ (perpendicular to a lattice plane with indices (hkl)) are of special importance. Therefore, the direction cosines of these vectors relative to the reference system $\{\mathbf{e}_1, \mathbf{e}_2, \mathbf{e}_3\}$ must be known. In TEV, the necessary transformations are calculated as follows (V and V^* are the unit cell volumes of the direct and the reciprocal lattice):

$$\mathbf{q}_{(hkl)} = \frac{\mathbf{r}^*}{|\mathbf{r}^*|} = \begin{pmatrix} \frac{1}{V b^* |\mathbf{r}^*|} \cdot (h c - l a \cos(\beta)) \\ \frac{1}{|\mathbf{r}^*|} \cdot (h a^* \cos(\gamma^*) + k b^* + l c^* \cos(\alpha^*)) \\ \frac{l}{c |\mathbf{r}^*|} \end{pmatrix}$$

$$\mathbf{q}_{[uvw]} = \frac{\mathbf{t}}{|\mathbf{t}|} = \begin{pmatrix} q_1 \\ q_2 \\ q_3 \end{pmatrix} = \begin{pmatrix} \frac{1}{V^* c |\mathbf{t}|} \cdot (u b^* - v a^* \cos(\gamma^*)) \\ \frac{v}{b^* |\mathbf{t}|} \\ \frac{1}{|\mathbf{t}|} \cdot (u a \cos(\beta) + v b \cos(\alpha) + w c) \end{pmatrix}$$

By plotting the thermal expansion coefficients α^{q_1, q_2, q_3} as a function of the direction $\mathbf{q} = (q_1, q_2, q_3)$ one obtains a geometric representation of the tensor in form of a surface in 3-D space. TEV calculates this representation surface and visualizes it as a surface chart.

Using the program – general remarks

The program allows you to determine the tensor of thermal expansion α_{ij} from

- (i) the evaluation of a data set containing a sequence of lattice parameters measured as a function of temperature T
- (ii) the evaluation of an already existing polynomial description of the lattice parameters obtained from *another* fitting program or from the literature

Remark: From version 1.0.1 onwards TEV is able to handle also more “sophisticated” expression that have been suggested in the literature including Einstein functions, Debye functions, two-term Einstein functions, two-term Debye functions, combinations between Einstein- and Debye functions or combinations between Einstein- and Debye functions with anharmonic contributions. For more details see Appendix I.

The experimental data for (i) must be stored in plain-text (ASCII) format. The file can be prepared with a standard text editor. People working with Excel or OpenOffice can simply save the data as character-separated values (CSV).

The data (without any header line) should have the following structure: the first column corresponds to the temperature T. Subsequent columns represent the numerical values of the unit cell parameters (real numbers with a “.” symbol for the decimal mark used to separate the integer from the fractional part). The lattice parameters can be given *either* with *or* without estimated standard uncertainties (e.s.u.). In case that the e.s.u. have been determined they can be provided directly following the fractional part of the relevant lattice parameters enclosed by round brackets “()”. For example, 9.335(12) corresponds to 9.335±0.012. If present, the e.s.u. will be used as weights for the least-squares fitting procedure of the polynomials. TEV will automatically recognize if e.s.u. have been provided or not. However, it is not allowed to use “mixed” data, i.e. lattice parameters with and without uncertainties cannot be contained within the same data set.

Data of different columns are separated by a “;” symbol. The number of columns depends on the crystallographic coordinate system:

| | |
|----------------------|--|
| Triclinic | $T_1; a_1; b_1; c_1; \alpha_1; \beta_1; \gamma_1$ |
| | $T_2; a_2; b_2; c_2; \alpha_2; \beta_2; \gamma_2$ |
| | \vdots |
| Monoclinic | $T_1; a_1; b_1; c_1; \text{oblique angle } \beta_1 \text{ or } \gamma_1$ |
| | $T_2; a_2; b_2; c_2; \text{oblique angle } \beta_2 \text{ or } \gamma_2$ |
| | \vdots |
| Orthorhombic | $T_1; a_1; b_1; c_1$ |
| | $T_2; a_2; b_2; c_2$ |
| | \vdots |
| Rhombohedral | $T_1; a_1; \alpha_1$ |
| | $T_2; a_2; \alpha_2$ |
| | \vdots |
| Hexagonal/Tetragonal | $T_1; a_1; c_1$ |
| | $T_2; a_2; c_2$ |
| | \vdots |
| Cubic | $T_1; a_1$ |
| | $T_2; a_2$ |
| | \vdots |

When entering already known polynomial coefficients for method **(ii)** these values must be separated by a vertical bar “|” (also referred to as the “pipe” symbol), i.e. the coefficients of the function $a(T) = p_0 + p_1 \cdot T + p_2 \cdot T^2 + p_3 \cdot T^3$ must be provided as $p_0 | p_1 | p_2 | p_3$.

For testing of option **(i)** three data sets (triclinic.crs, monoclinic.crs and hexagonal.crs) are available.

For testing of option **(ii)** already existing polynomials from the literature have been implemented as default values for the triclinic and monoclinic case. The triclinic data refer to the values given in the paper of Paufler & Weber (1999) and can be used for direct comparison of the results.

Option (i) : Steps for the evaluation of experimental data contained in a file

- Start the program
- Select the crystal system, e.g. monoclinic (in this specific case you must also check a radio button indicating if the oblique angle in the data set corresponds to β or γ)
- Select the temperature units ($^{\circ}\text{C}$ in this case) of the data set (via radio button)
- Select "Import experimental data" (via radio button)
- Select the example file "monoclinic.crs"
- Click on the "Next" button
- A window appears showing the evolution of the lattice parameter a as a function of T
- Fit $a(T)$ using a polynomial of first to fifth order by checking the corresponding radio buttons (the resulting coefficient of determination R^2 is calculated automatically)
- Select the next lattice parameter by clicking on the "b" flag (upper left corner of the window) and repeat the fitting procedure
- *Remark:* Different parameters can be fitted with polynomials of different orders
- Repeat these steps until ALL relevant lattice parameters have been fitted
- Click on the "Next" button
- A new window will pop up
- Enter the temperature of interest (default 25°C or 25 K)
- Click on the "Calculate CTE" button to activate all the calculations for the chosen temperature
- The tensor components are given for (i) the orthogonalized system $\{\mathbf{e}_1, \mathbf{e}_2, \mathbf{e}_3\}$ and (ii) after transformation to principal axes, i.e. referred to the system of eigenvectors $\{\mathbf{EV}_1, \mathbf{EV}_2, \mathbf{EV}_3\}$
- The angles between the vectors of the different coordinate systems $\{\mathbf{e}_1, \mathbf{e}_2, \mathbf{e}_3\}$, $\{\mathbf{EV}_1, \mathbf{EV}_2, \mathbf{EV}_3\}$ and $\{\mathbf{a}, \mathbf{b}, \mathbf{c}\}$ are determined
- A summary of the numerical output for the selected temperature (as well as the polynomial coefficients) can be copied to the clipboard ("Copy to clipboard" button)
- The whole calculations can be also performed automatically for a temperature interval in specific temperature steps. The numerical values for the start and the target temperature as well as the increment can be entered. Pressing the "Calculate" button activates the calculations. A window will pop up where the name of the export file can be entered. The calculated data are saved as character-separated values (CSV) in this file. Furthermore, the user can define the decimal separator used for the export as '.' or ',' via the corresponding radio buttons.

- In case that you want to calculate the value for the thermal expansion along a certain direction parallel to a lattice vector $[uvw]$ or perpendicular to a lattice plane with indices (hkl) you can enter the three integer values and click on the “Amplitude along $[uvw]$ ” or “Amplitude along reciprocal lattice vector...” button
- Click on the “Plot CTE” button to switch to the graphics part, where the representation surface of the tensor and specific sections can be visualized; the functions/options of this part should be obvious
- Click on the “Close” button
- Repeat the “Calculate CTE”, “Copy to clipboard” and “Plot CTE” steps for the corresponding temperatures of interest
- Finally, the content of the clipboard can be pasted into a text editor by the “Ctrl-v” sequence

Option (ii) : Steps for the evaluation of an already existing representation, e.g. polynomial

- Start the program
- Select the crystal system, e.g. triclinic
- Select the temperature units (K in this case) of the data (via radio button)
- Select "Literature data" (via radio button)
- A windows appears in which the known polynomial coefficients $p_0 - p_5$ can be entered for each lattice parameters
- For the triclinic and monoclinic case “default” values are provided corresponding to data from the literature which can be directly overwritten with your own values or used for testing (see above)
- Click on the “How to add polynomial coefficients ?” button to obtain some more information
- *Remark:* If you want to use only first or second order polynomials, enter only 2 or 3 values
- Click on the “Next” button
- A new window will pop up
- Enter the temperature of interest (default 25°C or 25 K)
- Click on the “Calculate CTE” button to activate all the calculations for the chosen temperature
- The tensor components are given for (i) the orthogonalized system $\{\mathbf{e}_1, \mathbf{e}_2, \mathbf{e}_3\}$ and (ii) after transformation to principal axes, i.e. referred to the system of eigenvectors $\{\mathbf{EV}_1, \mathbf{EV}_2, \mathbf{EV}_3\}$
- The angles between the vectors of the different coordinate systems $\{\mathbf{e}_1, \mathbf{e}_2, \mathbf{e}_3\}$, $\{\mathbf{EV}_1, \mathbf{EV}_2, \mathbf{EV}_3\}$ and $\{\mathbf{a}, \mathbf{b}, \mathbf{c}\}$ are determined
- A summary of the numerical output for the selected temperature (as well as the polynomial coefficients) can be copied to the clipboard (“Copy to clipboard” button)

- The whole calculations can be also performed automatically for a temperature interval in specific temperature steps. The numerical values for the start and the target temperature as well as the increment can be entered. Pressing the “Calculate” button activates the calculations. A window will pop up where the name of the export file can be entered. The calculated data are saved as character-separated values (CSV) in this file. Furthermore, the user can define the decimal separator used for the export as ‘.’ or ‘,’ via the corresponding radio buttons.
- In case that you want to calculate the value for the thermal expansion along a certain direction parallel to a lattice vector $[uvw]$ or perpendicular to a lattice plane with indices (hkl) you can enter the three integer values and click on the “Amplitude along $[uvw]$ ” or “Amplitude along reciprocal lattice vector...” button
- Click on the “Plot CTE” button to switch to the graphics part, where the representation surface of the tensor and specific sections can be visualized; the functions/options of this part should be obvious
- Click on the “Close” button
- Repeat the “Calculate CTE”, “Copy to clipboard” and “Plot CTE” steps for the corresponding temperatures of interest
- Finally, the content of the clipboard can be pasted into a text editor by the “Ctrl-v” sequence

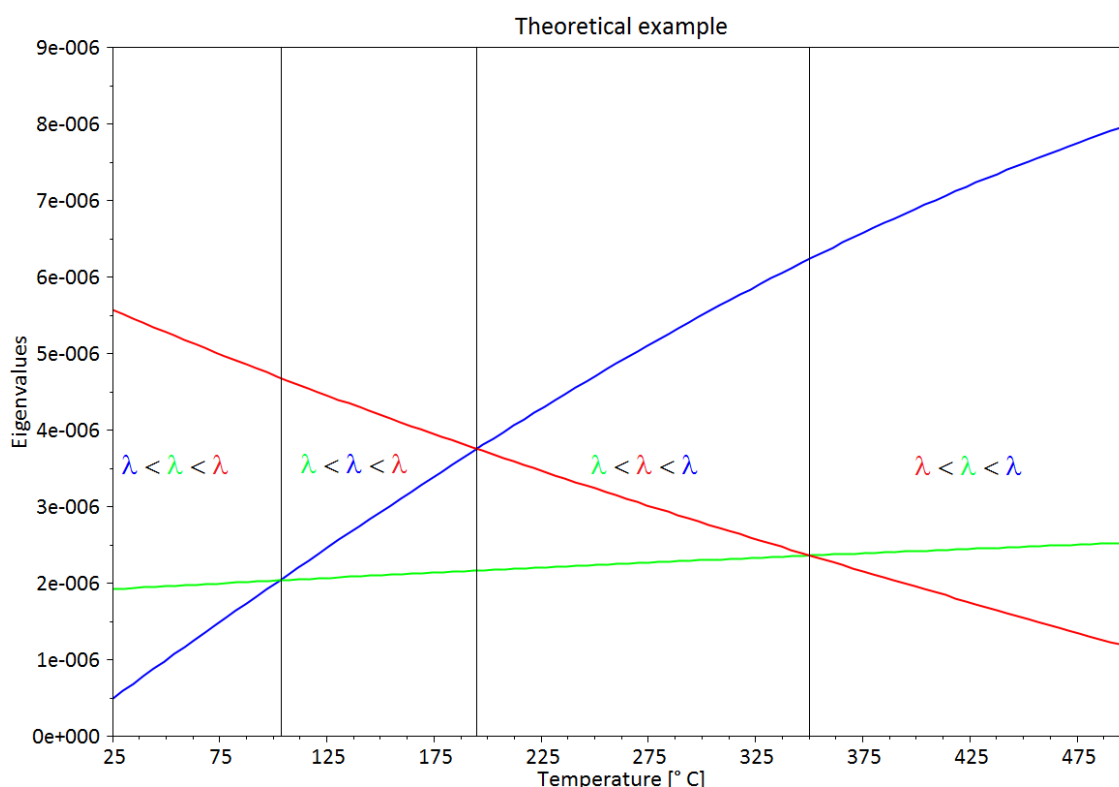
Final remarks:

A numerical description of the lattice parameters using polynomials is ONLY valid for the temperature interval for which experimental data have been collected. Therefore, it does not make any sense to use the program for the derivation of the thermal expansion tensor components or other related quantities for temperatures outside this interval.

Using the functions listed in Appendix I requires fitting of the data by non-linear least-squares which has to be performed *externally*. For this purpose the program Gnuplot (Williams et al., 2014) can be employed, for example, a public-domain package that is available for Linux, Windows and many other platforms. In order to facilitate this step we have provided demo scripts for this program on our homepage for each of the functions given in Appendix I. They can be easily adapted to a user-defined problem.

As may be anticipated, the calculations in the low symmetry crystal systems require special care. In the monoclinic case we derived some analytical expressions which are used for the determination of the eigenvalues and eigenvectors. For triclinic symmetry, the calculation of the magnitudes and directions of the principal axes is based on the Jacobi method for solving the corresponding matrix

equation. However, the user should keep in mind that in both systems there is always a certain degree of arbitrariness concerning the labeling of the eigenvalues (λ 's) and the eigenvectors (EV's). For monoclinic symmetry, λ_2 is related to $EV_2 = [010]$ (for second setting) and λ_3 to $EV_3 = [001]$ (for first setting), respectively. The labeling of the remaining two eigenvalues is performed in such a way that λ_1 corresponds to the smaller value, whereas λ_3 (or λ_2 , depending on the setting) is associated with the larger value. For a triclinic crystal the sequence of eigenvalues is always selected in such a way that $\lambda_1 < \lambda_2 < \lambda_3$. Apart from "pathological cases", where eigenvalues are accidentally equal for specific temperatures the above-mentioned approach for choosing the series of eigenvalues and vectors results in unique solutions for monoclinic and triclinic symmetry. Notably, however, the evolution of the values of specific eigenvalues as a function of temperature may change their order as well as the order of the eigenvectors. The following figure shows an artificial (and admittedly extreme) example for a triclinic crystal where the sequence of eigenvalues according to the criterion $\lambda_1 < \lambda_2 < \lambda_3$ would change four times within the temperature interval under investigation, i.e. whenever two of the $\lambda(T)$ -curves intersect.



Of course, the sequence of eigenvectors will change as well and, therefore, different labels will occur in the plots of the 3-D representation surface of the tensor and the sections depending on the temperature region under investigation. Furthermore, the user will observe apparent discontinuities for the angles between the crystallographic axes and the specific eigenvectors when crossing the

boundary between two temperature regions where the sequence changes. However, a critical check of the results will enable the identification these “pitfalls” easily.

Disclaimer

While we try to ensure that the TEV software is free of bugs and errors, people use this software at their own risk. We cannot accept any responsibility whatsoever for either incorrect results or for any damage arising from use of the software.

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Appendix I

Description of the more “sophisticated” fit functions for the evaluation of the temperature dependency of a lattice parameter p (p: a, b, c)

Einstein model

$$p(T) = p_0 + \frac{x_E}{\exp\left(\frac{\theta_E}{T}\right) - 1}$$

Fit parameters: p_0 , x_E and θ_E

Reference: Knight, K.S. (1996) *Mineral. Mag.*, 60, 963

Two-term Einstein model

$$p(T) = p_0 + \frac{x_{E1}}{\exp\left(\frac{\theta_{E1}}{T}\right) - 1} + \frac{x_{E2}}{\exp\left(\frac{\theta_{E2}}{T}\right) - 1}$$

Fit parameters: p_0 , x_{E1} , θ_{E1} , x_{E2} and θ_{E2}

Reference: Knight, K.S. (2012) *J. Solid State Chem.*, 194, 286.

Debye model

$$p(T) = p_0 + x_D \cdot T \cdot \frac{3}{\left(\frac{\theta_D}{T}\right)^3} \cdot \int_0^{\theta_D/T} \frac{t^3}{\exp(t) - 1} dt$$

Fit parameters: p_0 , x_D , and θ_D

Reference: Reference: Senyshyn, A., Trots, D.M., Engel, J.M., Vasylechko, L., Ehrenberg, H., Hansen, T., Berkowski, M. & Fuess, H. (2009) *J. Phys. Condens. Matter*, 21, 145405.

Two-term Debye model, weighted 1:2

$$p(T) = p_0 + x_{D1} \cdot T \cdot \frac{3}{\left(\frac{\theta_{D1}}{T}\right)^3} \cdot \int_0^{\theta_{D1}/T} \frac{t^3}{\exp(t) - 1} dt + x_{D2} \cdot T \cdot \frac{3}{\left(\frac{\theta_{D2}}{T}\right)^3} \cdot \int_0^{\theta_{D2}/T} \frac{t^3}{\exp(t) - 1} dt$$

Fit parameters: p_0 , x_{D1} , θ_{D1} , x_{D2} and θ_{D2} ; Constraint: $x_{D2} = \frac{1}{2} \cdot x_{D1}$

Reference: Knight, K.S. (2012) *J. Solid State Chem.*, 194, 286.

Einstein-Debye model

$$p(T) = p_0 + \frac{x_E}{\exp\left(\frac{\theta_E}{T}\right) - 1} + x_D \cdot T \cdot \frac{3}{\left(\frac{\theta_D}{T}\right)^3} \cdot \int_0^{\frac{\theta_D}{T}} \frac{t^3}{\exp(t) - 1} dt$$

Fit parameters: p_0 , x_E , θ_E , x_D and θ_D

Reference: Senyshyn, A., Boysen, H., Niewa, R., Banys, J., Kinka, M., Burak, Ya., Adamiv, V., Izumi, F., Chumak, I. & Fuess, H. (2012) *J. Phys. D Appl. Phys.*, 45, 175305.

Einstein-Debye model & anharmonic contributions

$$p(T) = p_0 + \frac{x_E}{\exp\left(\frac{\theta_E}{T}\right) - 1} + x_D \cdot T \cdot \frac{3}{\left(\frac{\theta_D}{T}\right)^3} \cdot \int_0^{\frac{\theta_D}{T}} \frac{t^3}{\exp(t) - 1} dt \\ + x_a \theta_D \frac{\exp\left(3 \frac{\theta_D}{T}\right) + 3\left(3 - 4 \frac{\theta_D}{T}\right) \exp\left(2 \frac{\theta_D}{T}\right) - 3\left(3 + 4 \frac{\theta_D}{T}\right) \exp\left(\frac{\theta_D}{T}\right) - 1}{\left(\exp\left(\frac{\theta_D}{T}\right) - 1\right)^3}$$

Fit parameters: p_0 , x_E , θ_E , x_D , θ_D and x_a

Reference: Reference: Senyshyn, A., Boysen, H., Niewa, R., Banys, J., Kinka, M., Burak, Ya., Adamiv, V., Izumi, F., Chumak, I. & Fuess, H. (2012) *J. Phys. D Appl. Phys.*, 45, 175305.

Cosine function for angles (φ : α, β, γ)

$$\varphi(T) = \varphi_0 + A \cdot \cos(B \cdot T)$$

Fit parameters: φ_0 , A and B

Reference: Knight, K.S., Stretton, I.C. & Schofield, P.F. (1999) *Phys. Chem. Minerals*, 26, 477.

“Saturation function” for angles (φ : α, β, γ)

$$\varphi(T) = \varphi_0 + A \cdot \left(1 - \exp(-B \cdot T)\right)^C$$

Fit parameters: φ_0 , A , B and C

Reference: Knight, K.S. & Price, G.D. (2008) *Can. Mineral.*, 46, 1593.

Remark:

Within the pre-defined Gnuplot scripts the following rational approximation was used for the calculation of the Debye function:

$$\frac{3}{x^3} \cdot \int_0^x \frac{t^3}{\exp(t) - 1} dt \cong \frac{1 + c_1 x + c_2 x^2}{1 + c_3 x + c_4 x^2 + c_5 x^3 + c_6 x^4 + c_5 \left(\frac{5}{\pi^4}\right) x^5}$$

$$c_1 = -0.07713, c_2 = 0.02433, c_3 = 0.30548, c_4 = 0.06513, c_5 = 0.03487, c_6 = -0.00324.$$

Reference: Masyukov, N.A. & Dmitriev, A.V. (2007) *Bull. Russ. Acad. Sci. Phys.*, 71, 1076.