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## TEV—A Program for the Determination of the Thermal Expansion Tensor from Diffraction Data

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Academic Editor: Anja-Verena Mudring

Received: 6 January 2015 / Accepted: 4 February 2015 / Published: 16 February 2015

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**Abstract:** TEV (Thermal Expansion Visualizing) is a user-friendly program for the calculation of the thermal expansion tensor  $\alpha_{ij}$  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  $\alpha_{ij}$  in the infinitesimal limit. The tensor components, eigenvalues, eigenvectors and their angles with the crystallographic axes can be evaluated for individual temperatures or for temperature ranges. Values of the tensor in 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 format. TEV is written in JAVA. 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. The program can be downloaded from the following link: <http://www.uibk.ac.at/mineralogie/downloads/TEV.html> (Institute of Mineralogy and Petrography, University of Innsbruck, Innsbruck, Austria)

**Keywords:** thermal expansion tensor; diffraction; representation surfaces; computer program

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## 1. Introduction

Together with thermal conductivity, thermal expansion is one of the key parameters for the physical characterization of the temperature dependent behavior of materials and is of relevance for both Earth and materials science. For anisotropic compounds such as crystalline phases which are uniformly heated or cooled the resulting homogeneous strain  $x_{ij}$  can be described by the following relationship:

$$x_{ij} = \alpha_{ij} \Delta T \quad (1)$$

where  $\alpha_{ij}$  are the thermal expansion coefficients defining a symmetrically second rank tensor and  $\Delta T$  is the temperature change. Most oxides, for example, have ambient temperature thermal expansion coefficients in the order of  $10^{-6}/\text{K}$ .

Classical methods for the evaluation of thermal expansion data include dilatometry (inductive, capacity, optical interference) or diffraction. Especially the last technique has been frequently employed for T-dependent investigations on single-crystals or polycrystalline compounds using X-rays or neutrons. According to Jessen and Küppers [1], two different approaches for the extraction of thermal expansion coefficients from diffraction data can be principally distinguished. In the first case, the inter-planar spacings  $d(hkl)$  of a set of  $m$  lattice planes  $(hkl)_m$  ( $m \gg 6$ ) is described by an appropriate function of temperature. Depending on the symmetry, the maximal six independent tensor components of  $\alpha_{ij}$  can be obtained from solving an over-determined system of  $m$  linear equations [2,3]. Alternatively, the changes in the lattice parameters  $a, b, c, \alpha, \beta, \gamma$  determined at different temperatures can be used directly to relate them to the tensor components  $\alpha_{ij}$  [4,5]. In reference [5], Schlenker *et al.* presented a mathematical treatment for the general triclinic case in terms of *finite* changes between two different temperatures  $T_1$  and  $T_2$ .

As discussed by Paufler and Weber [6], however, this methodology has the disadvantage that the consideration of finite temperature differences will always produce “average values”, while the magnitudes and the orientation of all three principal axes of the thermal expansion tensor for a triclinic crystal will change within the selected temperature interval without any coupling to the lattice parameters. Therefore, Paufler and Weber derived a set of equations that allow the calculation of the coefficients in the infinitesimal temperature limit.

In order to use this method the temperature dependency of the individual lattice-parameters has to be described by an appropriate function. In the literature, different mathematical expressions have been used for this purpose. A comparatively simple function is based on an Einstein model assuming that all atoms vibrate with the same angular frequency, *i.e.*, there exists a delta function in the phonon density of states at the Einstein frequency  $\omega_E$ . The resulting expression for the unit cell volume has been transferred to describe the temperature dependence of the individual unit cell edges:  $r(T) = r_0 + E/(\exp(\Theta_E/T) - 1)$ , where  $r_0$  (value for the particular lattice parameter  $r$  at  $T = 0$  K),  $\Theta_E$  (effective Einstein temperature) and  $E$  (Einstein constant) are the fit parameters [7–9]. For the description of more complex relationships between  $r$  and  $T$  “two-term Einstein models” [10,11], “extended Einstein-models” [12,13], Debye-like expressions [14] or combinations between Einstein- and Debye-like functions including anharmonic contributions [15] have been used. Alternatively, a more straightforward description using polynomials has also been successfully employed in many cases to model thermal expansion over large temperature intervals [6,16].

## 2. Results and Discussion

### 2.1. Mathematical Background

A second rank tensor (such as the tensor of thermal expansion  $\alpha_{ij}$ ) 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 in which 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:

$$\begin{pmatrix} \mathbf{a} \\ \mathbf{b} \\ \mathbf{c} \end{pmatrix} = \begin{pmatrix} a \sin \beta & 0 & a \cos \beta \\ -b \sin \alpha \cos \gamma^* & b \sin \alpha \sin \gamma^* & b \cos \alpha \\ 0 & 0 & c \end{pmatrix} \cdot \begin{pmatrix} \mathbf{e}_1 \\ \mathbf{e}_2 \\ \mathbf{e}_3 \end{pmatrix} \quad (2)$$

TEV is based on the abovementioned formalism of Paufler and Weber [6], where the temperature increments are treated in the infinitesimal limit. 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 the lattice parameter  $a$ , for example, for a third order polynomial can be parameterized as:

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

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

$$R^2 = \frac{\sum_{i=1}^n (a_i - \bar{a})^2 - \sum_{i=1}^n (a_i - \hat{a}_i)^2}{\sum_{i=1}^n (a_i - \bar{a})^2} \quad (4)$$

( $a_i$ : 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 (for the most general triclinic case) independent  $\alpha_{ij}$  components can be related to the lattice parameters and their derivatives according to the following mathematical expressions presented by Paufler and Weber [6]:

$$\alpha_{11} \approx \frac{1}{a} \frac{da}{dT} + \frac{d\beta}{dT} \cot \beta \quad (5)$$

$$\alpha_{22} \approx \frac{1}{b} \frac{db}{dT} + \frac{d\alpha}{dT} \cot \alpha + \frac{d\gamma^*}{dT} \cot \gamma^* \quad (6)$$

$$\alpha_{33} \approx \frac{1}{c} \frac{dc}{dT} \quad (7)$$

$$\alpha_{12} \approx \frac{1}{2} \cot \gamma^* \left( \frac{1}{a} \frac{da}{dT} - \frac{1}{b} \frac{db}{dT} - \frac{d\alpha}{dT} \cot \alpha + \frac{d\beta}{dT} \cot \beta \right) + \frac{1}{2} \frac{d\gamma^*}{dT} \quad (8)$$

$$\alpha_{13} \approx \frac{1}{2} \left( \frac{1}{a} \frac{da}{dT} - \frac{1}{c} \frac{dc}{dT} \right) \cot \beta - \frac{1}{2} \frac{d\beta}{dT} \quad (9)$$

$$\alpha_{23} \approx \frac{1}{2} \left( \left( \frac{1}{a} \frac{da}{dT} - \frac{1}{c} \frac{dc}{dT} \right) \cot \gamma^* \cot \beta + \left( \frac{1}{b} \frac{db}{dT} - \frac{1}{c} \frac{dc}{dT} \right) \frac{\cot \alpha}{\sin \gamma^*} - \left( \frac{1}{\sin \gamma^*} \frac{d\alpha}{dT} + \frac{d\beta}{dT} \cot \gamma^* \right) \right) \quad (10)$$

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  $a$ ,  $b$ ,  $c$ ,  $\alpha$ ,  $\beta$  and  $\gamma$ .

Using the components of the symmetrical  $\alpha_{ij}$ -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  $\{\mathbf{e}_1, \mathbf{e}_2, \mathbf{e}_3\}$ :

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

Frequently, the values of  $\alpha_{ij}$  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, respectively):

$$\mathbf{q}_{(hkl)} = \frac{\mathbf{r}^*}{|\mathbf{r}^*|} = \begin{pmatrix} q_1 \\ q_2 \\ q_3 \end{pmatrix} = \begin{pmatrix} \frac{1}{Vb^*|\mathbf{r}^*|} \cdot (hc - la\cos\beta) \\ \frac{1}{|\mathbf{r}^*|} \cdot (ha^*\cos\gamma^* + kb^* + lc^*\cos\alpha^*) \\ \frac{l}{c|\mathbf{r}^*|} \end{pmatrix} \quad (12)$$

$$\mathbf{q}_{[uvw]} = \frac{\mathbf{t}}{|\mathbf{t}|} = \begin{pmatrix} q_1 \\ q_2 \\ q_3 \end{pmatrix} = \begin{pmatrix} \frac{1}{V^*c|\mathbf{t}|} \cdot (ub^* - va^*\cos\gamma^*) \\ \frac{v}{b^*|\mathbf{t}|} \\ \frac{1}{|\mathbf{t}|} \cdot (ua\cos\beta + vb\cos\alpha + wc) \end{pmatrix} \quad (13)$$

By plotting the thermal expansion coefficients  $\alpha^{q_1, q_2, q_3}$  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. Alternatively, pre- or user-defined 2-D sections can be drawn. The corresponding figures can be exported in bitmap format (PNG).

## 2.2. Using the Program—General Remarks

The program allows the user to determine the tensor of thermal expansion  $\alpha_{ij}$  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.

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 the 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  $9.335 \pm 0.012$ . If present, the e.s.u. will be used as weights for the least-squares fitting procedure of the polynomials. TEV will automatically recognize whether 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:

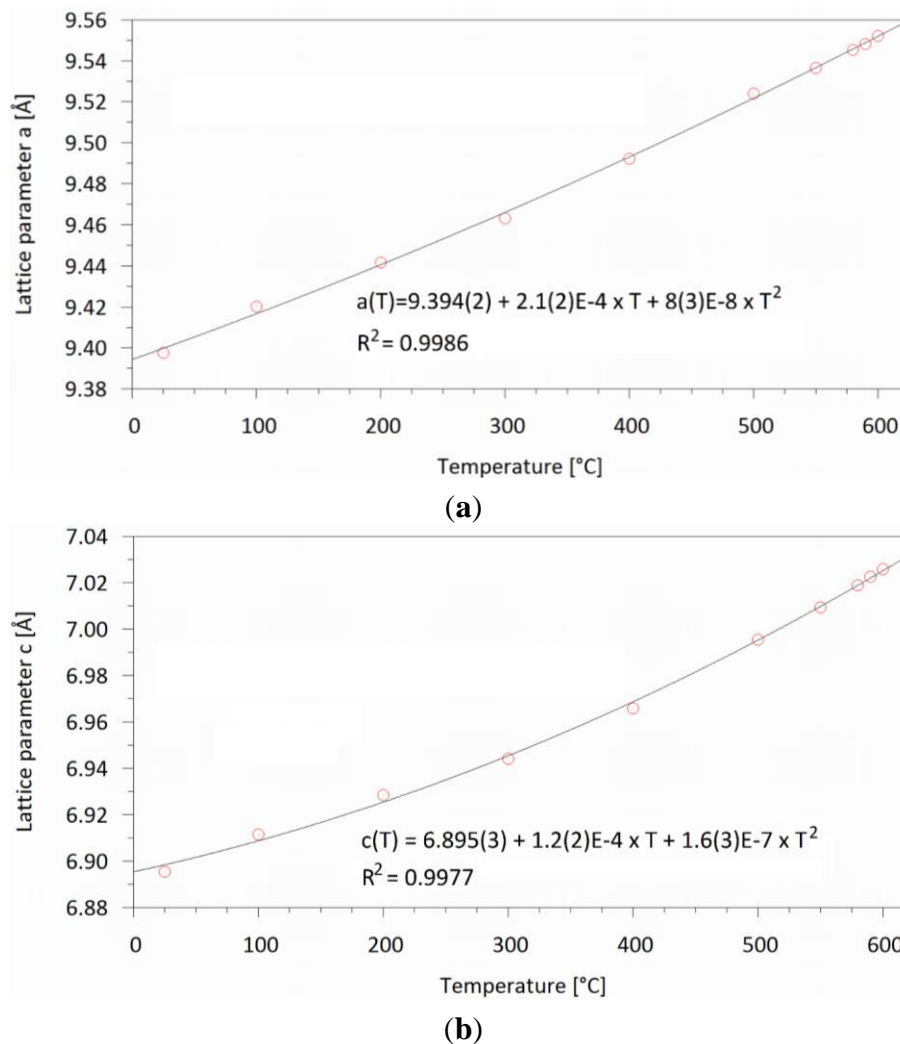
Triclinic	$T_1; a_1; b_1; c_1; \alpha_1; \beta_1; \gamma_1$
	$T_2; a_2; b_2; c_2; \alpha_2; \beta_2; \gamma_2$
	$\vdots$
Monoclinic	$T_1; a_1; b_1; c_1; \text{oblique angle } \beta_1 \text{ or } \gamma_1$
	$T_2; a_2; b_2; c_2; \text{oblique angle } \beta_2 \text{ or } \gamma_2$
	$\vdots$
Orthorhombic	$T_1; a_1; b_1; c_1$
	$T_2; a_2; b_2; c_2$
	$\vdots$
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 (triclinicESU.crs, monoclinic.crs and hexagonal.crs) are available. For testing of option (ii), 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 and Weber [6] and can be used for direct comparison of the results.

### 2.3. Examples

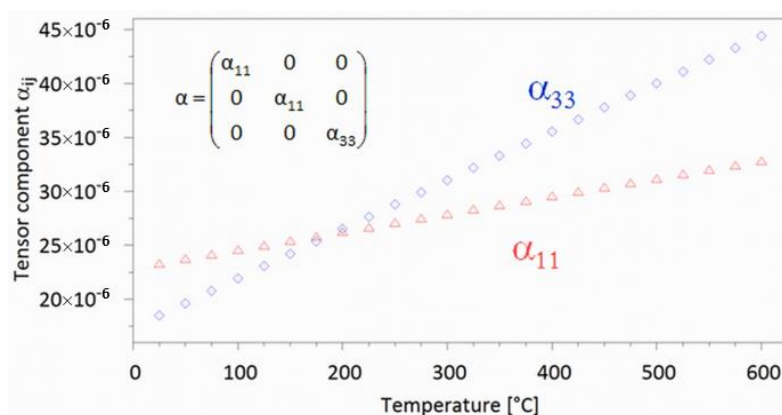
The data of the first example refer to the *high-temperature* behavior of a hexagonal sulfate apatite with composition  $\text{Na}_2\text{Ca}_3(\text{SO}_4)_3\text{F}$  [17] (point group 6/m). In the range between 25 °C and 600 °C both lattice parameters were fitted with second-order polynomials (see Figure 1).



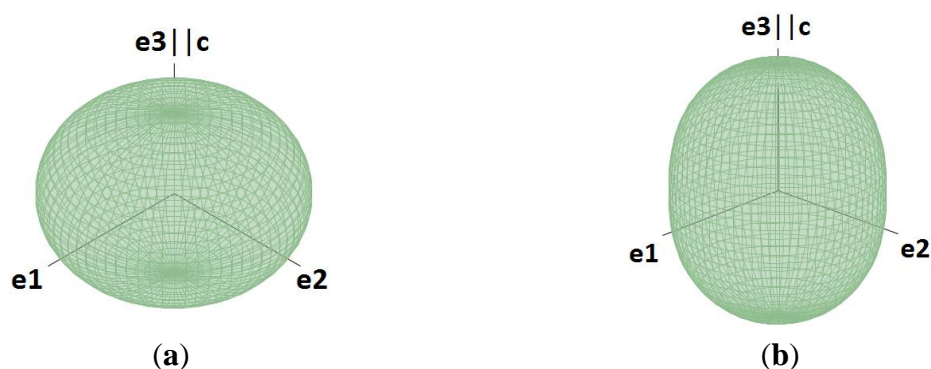
**Figure 1.** Evolution of the (a)  $a$ -; and (b)  $c$ -lattice parameters for hexagonal  $\text{Na}_2\text{Ca}_3(\text{SO}_4)_3\text{F}$ .

Subsequently, the evolution of the two symmetry independent tensor components  $\alpha_{11}$  and  $\alpha_{33}$  has been calculated in steps 25 °C. It is obvious from Figure 2 that at temperatures below  $\approx 190$  °C the thermal expansion parallel to [001] is smaller than perpendicular to [001]. Above 190 °C, however, this trend is reversed. This observation is also reflected in the comparison between the shapes of the representation surfaces at ambient temperature and 600 °C, for example, which change from an oblate to a prolate form (see Figure 3). For hexagonal symmetry, these surfaces must be rotationally symmetric along the direction of the sixfold rotation axis of the point group.

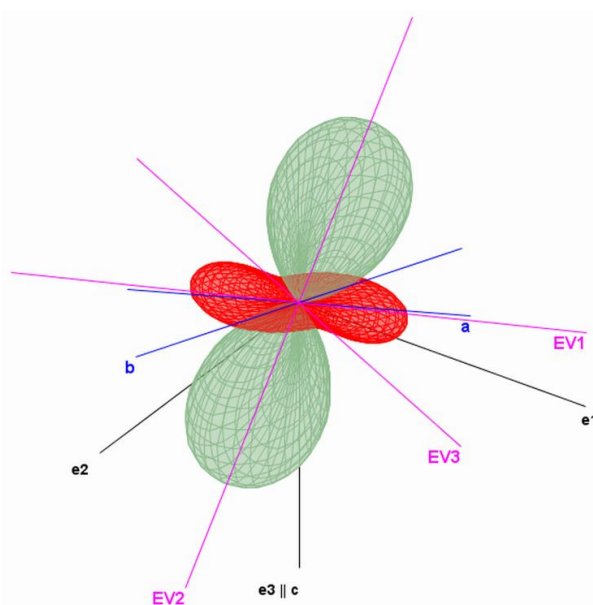
The second example is based on the *low-temperature* investigations of Weber *et al.* [18] on triclinic  $\alpha\text{-CuMoO}_4$  (point group  $\bar{1}$ ). The coefficients of the polynomials up to third order for all six metrical parameters have been directly taken from their publication. The following Figure 4 shows the 3-D representation surface of the thermal expansion tensor for 70 K.



**Figure 2.** Temperature dependency of  $\alpha_{11}$  and  $\alpha_{33}$ . The figure has been produced from the numerical output of Thermal Expansion Visualizing (TEV) using the program Gnuplot [19].

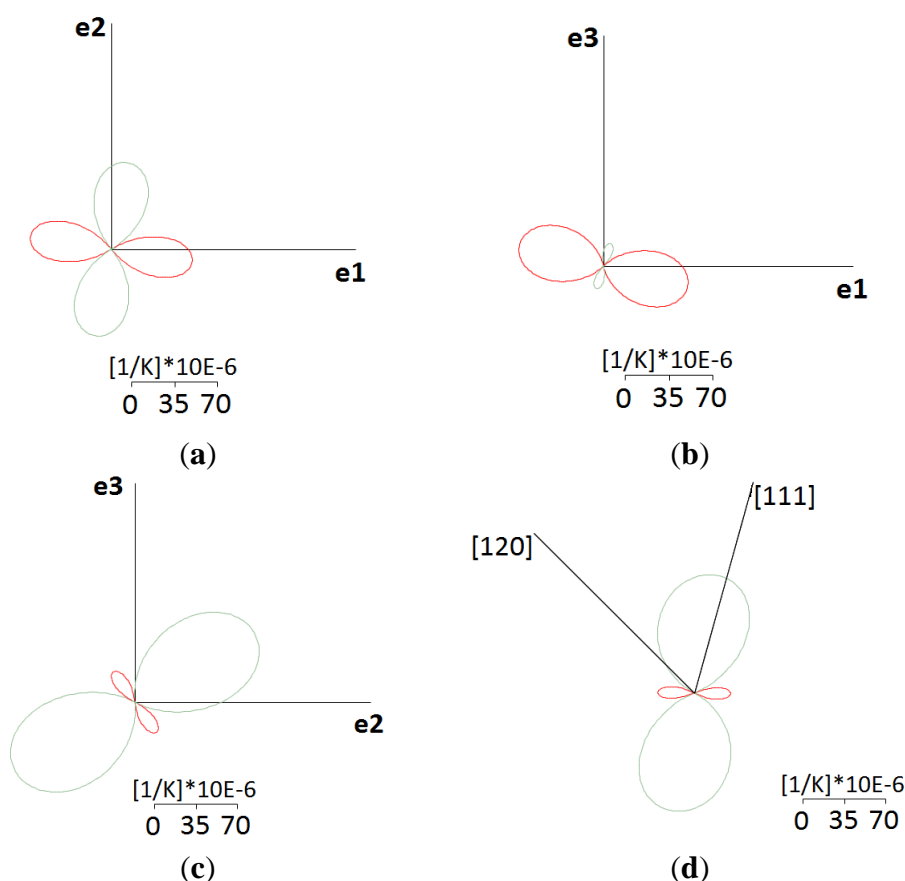


**Figure 3.** Representation surfaces for the tensor of thermal expansion at (a) 25  $^{\circ}\text{C}$ ; and (b) 600  $^{\circ}\text{C}$ .



**Figure 4.** Representation surface of the thermal expansion tensor for  $\alpha$ -CuMoO<sub>4</sub> at 70 K. Red parts of the surface indicate directions with negative values of thermal expansion. The crystallographic system  $\{a, b, c\}$ , the orthonormal system  $\{e_1, e_2, e_3\}$  and the coordinate system of the eigenvectors  $\{EV1, EV2, EV3\}$  are indicated as well.

For the interpretation of the tensor data it is often helpful to consider sections through the 3-D representation surface. The Figure 5a–d shows the corresponding default sections (defined by the  $\mathbf{e}_1$ - $\mathbf{e}_2$ ,  $\mathbf{e}_2$ - $\mathbf{e}_3$ ,  $\mathbf{e}_3$ - $\mathbf{e}_1$  planes) and a section that was explicitly defined by the two crystallographic directions [111] and [120], for example. The latter option can be of special interest for the interpretation of thermal expansion data in terms of the atomic arrangements in a given crystal structures, e.g., anisotropy of thermal expansion within a specific plane defined by layer-like building units. Surface plots and sections can be saved in a bitmap format (PNG).



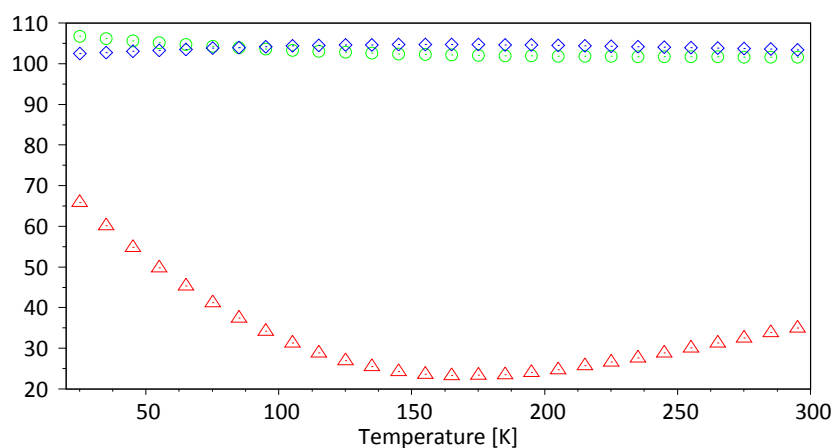
**Figure 5.** Three default (a–c) and specific (d) sections through the 3-D representation surface for  $\alpha$ -CuMoO<sub>4</sub> at 70 K.

The variation of the orientation of the thermal expansion tensor with temperature can be observed in the changes of the angles between the eigenvectors  $\{\mathbf{EV1}, \mathbf{EV2}, \mathbf{EV3}\}$  and the crystallographic axes  $\{\mathbf{a}, \mathbf{b}, \mathbf{c}\}$ , for example. Figure 6 shows the temperature dependency of the angle between eigenvector  $\mathbf{EV2}$  and the three basis vectors  $\{\mathbf{a}, \mathbf{b}, \mathbf{c}\}$ . While  $\angle(\mathbf{EV2}, \mathbf{b})$  and  $\angle(\mathbf{EV2}, \mathbf{c})$  show only relatively small changes as a function of  $T$ , the angle  $\angle(\mathbf{EV2}, \mathbf{a})$  exhibits a strong variation and a pronounced non-linear behavior.

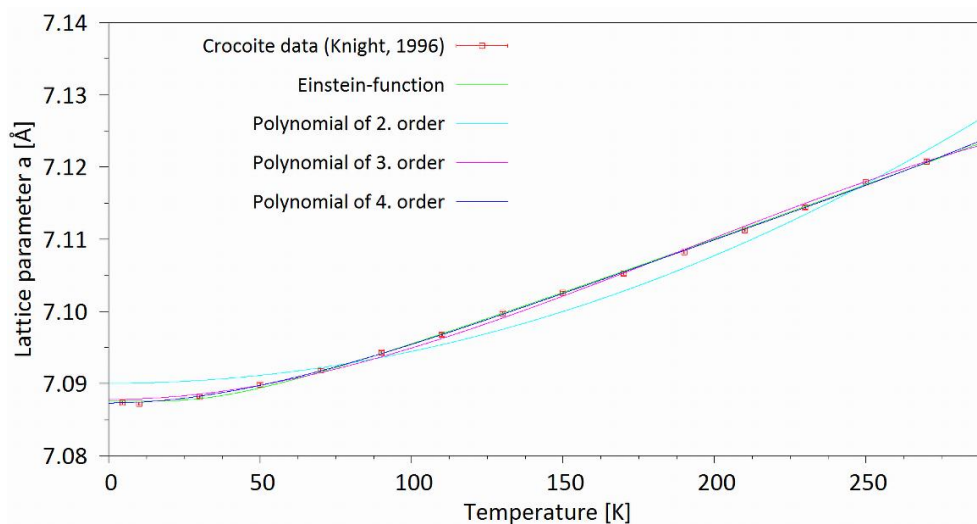
According to our own investigations on the high-temperature behavior of oxide materials polynomials of second order are in many cases sufficient for the description of the lattice parameters as a function of  $T$ . However, for low-temperature data sets with data points close to absolute zero higher orders may be necessary. Figure 7 shows the temperature dependency of the  $a$  unit cell parameter of monoclinic crocoite (PbCrO<sub>4</sub>) taken from Knight [7]. For comparison, data were fitted using an Einstein-function



with three variable parameters as well as polynomials of orders two, three and four. In this case fitting was performed with the program Gnuplot [19]. It is obvious that a second order polynomial cannot be used to model the data adequately. However, the inclusion of third and fourth order terms resulted in a fit that is almost indistinguishable from the Einstein function. In summary, one can say that polynomial functions offer a great variability of applications concerning the coverage of different temperature regions.



**Figure 6.** Variation of the angle between eigenvector **EV2** and **a** (triangles), **b** (spheres) and **c** (rhombs) for the T-range from 20 to 300 K.



**Figure 7.** Comparison between an Einstein-type function and polynomials of order two, three and four for the modeling of the low-temperature behavior of the *a* lattice parameter of crocoite (PbCrO<sub>4</sub>).

#### 2.4. Final Remarks

In the present TEV version 0.9.4 only polynomials can be used for the evaluation of the T-dependence of the lattice parameters. The user should keep in mind that this description 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. An extended version of the program which will include

other expressions for fitting such as Einstein- or Debye-functions is currently in progress. Furthermore, it is worth mentioning that compressibilities derived from pressure dependent diffraction data are second rank tensors as well and could be principally visualized using the same approach although other expressions such as Birch-Murnaghan equations of state of different orders have to be used for this purpose. This topic may be addressed in future versions.

TEV is written in JAVA. The program uses several libraries that are listed under the menu point “Help”. A pre-requisite for working with TEV is the installation of the JAVA runtime environment of at least version 7 which can be downloaded from the following link: <http://www.java.com/en/download/> [20]. 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 and several license files for the libraries are included. The distribution can be downloaded from the following link: <http://www.uibk.ac.at/mineralogie/downloads/TEV.html> [21].

## Acknowledgments

The authors are thankful for the comments and suggestions of three anonymous reviewers.

## Author Contributions

Thomas Langreiter wrote the program TEV as a part of his Master thesis. Volker Kahlenberg conceived and designed the project.

## Conflicts of Interest

The authors declare no conflict of interest.

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