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Algorithm for Calculating the Thermal Expansion Tensor and Constructing the Thermal Expansion Diagram for Crystals

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Abstract—A new program package based on the Microsoft Windows operational systems is proposed for thermal investigations of crystals. The package consists of two programs, one of which provides a means for calculating the thermal expansion tensor for crystals of any symmetry and the second program is intended for drawing three-dimensional thermal expansion diagrams. The calculation and drawing procedures are described.

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INTRODUCTION

The temperature dependence of the lattice parameters (unit cell parameters, interplanar spacings) and the crystal structure parameters (atomic coordinates, bond lengths, bond angles, etc.) can serve as a characteristic of thermal expansion of crystals. As a rule, this dependence can be approximated by polynomials of the type $P(T) = A_0 + A_1T + A_2T^2 + \dots$. These are first- or second-order polynomials in the majority of cases and higher order polynomials in rare cases. Crystals undergo deformation with a variation in the temperature. Most frequently, thermal variations in the unit cell parameters and the unit cell volume are described using the thermal expansion coefficient. For example, for an arbitrary lattice parameter l , we have

$$\alpha_l = \varepsilon_l/dT = (dl/l)/dT,$$

where α_l is the thermal expansion coefficient for the parameter l , $\varepsilon_l = dl/l$ is the strain for the parameter l , and T is the temperature. Therefore, the thermal expansion coefficient characterizes the temperature dependence of the strain.

The thermal expansion coefficient of the crystal can be easily calculated from the polynomial that represents the lattice parameter as a function of the temperature. However, in the general case, these data do not allow one to describe completely the thermal behavior of the crystal.

It is known that the strain in crystals is described by a second-rank tensor ε and, correspondingly, the depen-

dence of the strain on the scalar parameter T is also represented by the second-rank tensor

$$\alpha = \begin{pmatrix} \alpha_{11} & \alpha_{12} & \alpha_{13} \\ \alpha_{21} & \alpha_{22} & \alpha_{23} \\ \alpha_{31} & \alpha_{32} & \alpha_{33} \end{pmatrix}.$$

It is more convenient to represent the tensor in the form reduced to the principal axes, i.e., in the Cartesian coordinate system in which the tensor is described by the diagonal matrix

$$\alpha = \begin{pmatrix} \alpha_1 & 0 & 0 \\ 0 & \alpha_2 & 0 \\ 0 & 0 & \alpha_3 \end{pmatrix}.$$

Each component of the thermal expansion tensor and the corresponding component of the strain tensor are related through the temperature; that is,

$$\varepsilon_{ij} = \alpha_{ij}dT.$$

The crystal symmetry imposes limitations on the thermal expansion tensor [1]. In crystals of the cubic crystal system, all diagonal components of the thermal expansion tensor (α_{11} , α_{22} , α_{33}) are equal to each other, the other components are identically equal to zero, and the principal axes can be chosen in an arbitrary manner (it is common practice to choose them in parallel to the crystallographic axes). In this case, in order to describe completely the thermal behavior, it is sufficient to calculate the thermal expansion coefficient in one arbitrarily chosen direction.

In crystals of the hexagonal, trigonal, and tetragonal crystal systems, one tensor axis is oriented parallel to the higher order symmetry axis (the c axis), and the other two axes (equivalent to each other) are arbitrarily chosen in the plane normal to the c axis. The thermal expansion can be completely described by the thermal expansion coefficients along the c axis and in any direction normal to this axis.

In orthorhombic crystals, the tensor axes are always parallel to the mutually perpendicular crystallographic axes. The thermal expansion coefficients along these axes are the eigenvalues of the thermal expansion tensor.

Crystals of the oblique crystal systems (monoclinic, triclinic) occupy a special place. In this case, the problem associated with the determination of orientation of the principal axes and the principal components of the thermal expansion tensor is not so trivial. The solution of this problem requires additional calculations, and researchers often restrict themselves only to the calculation of the thermal expansion coefficients along the crystallographic axes (see, for example, [2]). This approach for a long time did not permit one to reveal the frequently observed negative thermal expansion (more recently described in [3]) and, in general, provides incomplete information on the thermal behavior of crystals.

When investigating the thermal expansion of crystals, there exists one more problem that consists in constructing the thermal expansion diagram, whose graphical representation makes it possible to visualize qualitatively and quantitatively the thermal expansion anisotropy of crystals.

The thermal expansion diagram is an indicatrix of the tensor. The magnitudes of the radius vectors of the points at the indicatrix indicate the magnitude (coefficient) of thermal expansion in the direction of this radius vector.

A.V. Shubnikov [4] proved that the thermal expansion diagram is a sixth-order surface and described all types of diagrams possible in crystals. In the case of the tensor reduced to the principal axes, the thermal expansion diagram can be analytically represented in the form

$$(\alpha_1 x^2 + \alpha_2 y^2 + \alpha_3 z^2)^2 = (x^2 + y^2 + z^2)^3.$$

It is difficult to construct these surfaces by hand because of the complex shape and the complex analytical expression. However, the techniques of modern three-dimensional computer graphics provide a means of drawing these surfaces according to a very simple algorithm.

In the present work, we developed the computer program DTC (Deformation Tensor Computing) for determining the values and orientation of the thermal expansion tensor in the general case of a triclinic crystal and the program DTP (Deformation Tensor Plot) for

drawing the three-dimensional thermal expansion diagrams.

ALGORITHM FOR CALCULATING THE THERMAL EXPANSION TENSOR IN THE GENERAL CASE OF A TRICLINIC CRYSTAL

In the developed program, we used the algorithm that enables one to calculate the tensor components and the orientation of the principal axes of the tensor at a particular temperature from the temperature dependences of the unit cell parameters.

In the framework of the algorithm, the dependences of the unit cell parameters (having the first derivative with respect to the temperature),

$$a = a(T), \quad b = b(T), \quad c = c(T), \\ \alpha = \alpha(T), \quad \beta = \beta(T), \quad \gamma = \gamma(T),$$

should be introduced at the input.

In this case, for these functions, it is possible to determine the derivatives da/dT , db/dT , dc/dT , $d\alpha/dT$, $d\beta/dT$, and $d\gamma/dT$.

In the monographs [5, 6], the formulas are presented for the calculation of the interplanar spacing in the form d_{hkl}^{-2} as a function f of the indices h , k , and l and the unit cell parameters

$$d_{hkl}^{-2} = f(h, k, l, a, b, c, \alpha, \beta, \gamma),$$

where d_{hkl} is the interplanar spacing for the series of planes with the indices h , k , and l .

At fixed indices h , k , and l , this equation is used to calculate the quantity d_{hkl}^2 and the partial derivatives of the function f at known values of a , b , etc. By differentiating the right- and left-hand sides of this equation, we find

$$-2d_{hkl}^{-3} dd_{hkl} = (\partial f / \partial a) da + (\partial f / \partial b) db + (\partial f / \partial c) dc \\ + (\partial f / \partial \alpha) d\alpha + (\partial f / \partial \beta) d\beta + (\partial f / \partial \gamma) d\gamma.$$

Now, the equation is divided by dT and multiplied into $(-d_{hkl}^2/2)$. As a result, we obtain

$$\frac{dd_{hkl}}{d_{hkl}dT} = \frac{-d_{hkl}^2}{2} \left(\frac{\partial f}{\partial a} \frac{da}{dT} + \frac{\partial f}{\partial b} \frac{db}{dT} + \frac{\partial f}{\partial c} \frac{dc}{dT} \right. \\ \left. + \frac{\partial f}{\partial \alpha} \frac{d\alpha}{dT} + \frac{\partial f}{\partial \beta} \frac{d\beta}{dT} + \frac{\partial f}{\partial \gamma} \frac{d\gamma}{dT} \right).$$

In the last equation, the left-hand side is the thermal expansion coefficient α_d for the interplanar spacing. The right-hand side can be easily calculated, because all its components d_{hkl}^2 , $(\partial f / \partial a)$, da/dT , and others are already known.

Calculated parameters characterizing the thermal expansion of the bismuth barium borate $\text{BaBi}_2\text{B}_4\text{O}_{10}$ (the output from the DTC program)

Parameters	Temperature, °C				
	0	25	50	75	100
	Values of the parameters				
α_1	-3.64E-06	-2.26E-06	-8.85E-07	4.72E-07	1.81E-06
α_2	7.85E-06	7.85E-06	7.84E-06	7.84E-06	7.84E-06
α_3	1.29E-05	1.28E-05	1.28E-05	1.27E-05	1.27E-05
$\mu_{3c}, ^\circ$	5.722	4.8	3.53	2.043	0.2177
α_V	1.71E-05	1.84E-05	1.98E-05	2.11E-05	2.24E-05
α_α	-1.97E-06	-8.86E-07	1.97E-07	1.28E-06	2.36E-06
α_b	7.85E-06	7.85E-06	7.84E-06	7.84E-06	7.84E-06
α_c	1.27E-05	1.27E-05	1.27E-05	1.27E-05	1.27E-05
α_β	3.70E-06	3.11E-06	2.53E-06	1.95E-06	1.36E-06

Designations: α_1 , α_2 , and α_3 are the tensor components along the principal axes; μ_{ip} is the angle between the i th axis of the tensor and the p crystallographic axis (positive upon counterclockwise rotation); $\alpha_a, \dots, \alpha_V$ are the thermal expansion coefficients for the unit cell parameters and the unit cell volume; and E-06 = 10^{-6} .

Hereafter, we will use the crystal physical coordinate system in which $\mathbf{X} \parallel \mathbf{a}^*$, $\mathbf{Z} \parallel \mathbf{c}^*$, and the axis \mathbf{Y} lies in the plane of the vectors \mathbf{a}^* and \mathbf{b}^* . In this case, the direction cosines of the normal to the series of the planes under consideration are calculated by formulas [3]

$$x_d = \frac{h|\mathbf{a}^*| + k|\mathbf{b}^*|\cos\gamma^* + l|\mathbf{c}^*|\cos\beta^*}{|\mathbf{H}_{hkl}|}$$

$$y_d = \frac{k|\mathbf{b}^*|\sin^2\gamma^* + l|\mathbf{c}^*|(\cos\alpha^* - \cos\gamma^*\cos\beta^*)}{\sin\gamma^*|\mathbf{H}_{hkl}|}$$

$$z_d = \frac{l|\mathbf{c}^*|\cos(\widehat{\mathbf{cc}^*})}{|\mathbf{H}_{hkl}|} = \frac{l|\mathbf{c}^*|\sin\alpha\sin\beta^*}{|\mathbf{H}_{hkl}|},$$

where x_d , y_d , and z_d are the direction cosines of the normal along the crystallographic axes X , Y , Z , respectively; \mathbf{a} , \mathbf{b} , and \mathbf{c} are the vectors of the unit cell parameters; α , β , and γ are the angular parameters of the unit cell; \mathbf{a}^* , \mathbf{b}^* , and \mathbf{c}^* are the vectors of the reciprocal lattice; α^* , β^* , and γ^* are the angular parameters of the reciprocal lattice; and $\mathbf{H}_{hkl} = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^*$.

The equation that relates the thermal expansion along the interplanar spacing under consideration and the thermal expansion tensor can be written in the following form:

$$\alpha_d = \alpha_{11}x_d^2 + \alpha_{22}y_d^2 + \alpha_{33}z_d^2 + 2\alpha_{12}x_dy_d + 2\alpha_{23}y_dz_d + 2\alpha_{13}x_dz_d, \quad (*)$$

where α_{ij} are six independent components of the thermal strain tensor (in the crystal physical coordinate system) to be determined.

It is always possible to construct six linearly independent equations of the type of Eq. (*) for six different series of planes and, thus, to obtain an inhomogeneous system of linear equations with six unknowns. For example, in the DTC program, the equations are constructed for the planes (100), (010), (001), (110), (101), and (011). Since the equations are linearly independent, this system always has a unique solution, which consists of all six independent components of the thermal expansion tensor in the crystal physical coordinate system.

The orientation of the principal axes of the tensor can be determined by different methods, for example, by solving homogeneous equations according to the procedure described in [7]. In the DTC program, we used the elementary Jacobi rotation algorithm [8].

THE DTC (DEFORMATION TENSOR COMPUTING) PROGRAM

The DTC program is intended for calculating the thermal expansion tensor of crystals from the polynomial dependences of the unit cell parameters on the temperature. However, this program can also be used to calculate the tensors of compression under pressure and other types of deformations by replacing the temperature by another variable parameter in the polynomial describing the unit cell parameters. The program is written for the use in the modern Microsoft Windows operational systems based on the NET technology. For the systems developed earlier than the Windows Vista, it is necessary to install the Microsoft.NET Framework 2.0.

The initial data for the calculation are the coefficients of the polynomials approximating the temperature dependence of the unit cell parameters and the tem-

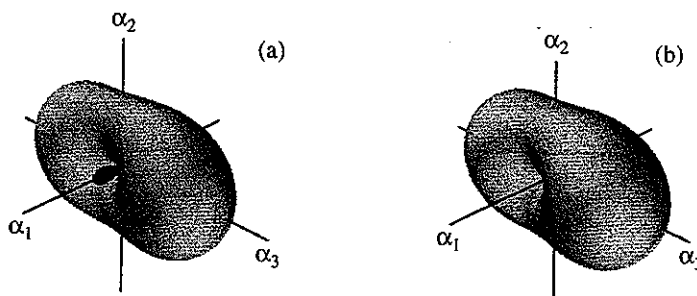


Fig. 1. Thermal expansion diagrams constructed with the DTP program for temperatures of (a) 0 and (b) 100°C.

peratures of interest to a user. The highest degree of polynomials in the program is equal to five. For convenience of operation with the data, the user should introduce the crystal system of the crystal under investigation.

The results of calculations are output in the form of the table including quantities calculated at the temperatures specified by the user. The program makes it possible to print out the results on a printer or to write them in the form of the HTML file, which can be processed using other programs.

For the repeated use of the entered data, the user can save them and load from the files with the extension .dtc. The format of the dtc-files is based on the XML format with the XML Schema definition.

THE DTP (DEFORMATION TENSOR PLOT) PROGRAM

The developed package involves the DTC program described above and the DTP (Deformation Tensor Plot) program for drawing three-dimensional thermal expansion diagrams. This program operates according to the following simple algorithm.

It is necessary to construct a unit-radius sphere in the three-dimensional space from the array of points (x' , y' , z'). Then for each point of the array, the thermal expansion coefficient α_r along the radius vector of the sphere is calculated by the formula

$$\alpha_r = \alpha_{11}x'^2 + \alpha_{22}y'^2 + \alpha_{33}z'^2.$$

Since the coordinates of each point x , y , z in the unit sphere are equal to the direction cosines of its radius vector, it is easy to determine the location of the point in the indicatrix of the tensor; that is,

$$x = \alpha_r x', \quad y = \alpha_r y', \quad z = \alpha_r z',$$

where (x, y, z) is the point at the surface of the thermal expansion diagram and (x', y', z') is the point at the surface of the unit sphere.

Therefore, the array of points of the unit sphere is transformed into the array of points of the thermal expansion diagram.

In the DTP program, in order to construct the indicatrix, it is necessary to enter only the tensor components along the principal axes. As a result, the program displays the window with the three-dimensional image of the sought surface in the form of the perspective projection. The program allows one to export the image to a raster file in either of two formats: .jpg or .bmp.

Examples

The use of the DTC and DTP programs can be illustrated using the following data on the thermal expansion for $\text{BaBi}_2\text{B}_4\text{O}_{10}$ compound [9]:

$$a(t) = 10.156 - 0.00002t + 0.00000022t^2,$$

$$b(t) = 6.371(1) + 0.000050(4)t,$$

$$c(t) = 12.475(2) + 0.000159(5)t,$$

$$\beta(t) = 102.76(2) + 0.00038(15)t - 0.0000012(2)t^2,$$

$$V(t) = 784.3(2) + 0.0309(6)t.$$

The results of calculation performed with the DTC program are presented in the table. The thermal expansion diagram constructed with the DTP program for temperatures of 0 and 100°C is shown in the figure.

The temperature dependence of each thermal expansion coefficient can be represented in the form of the polynomial $\alpha(T) = A_0 + A_1T + A_2T^2 + \dots$ with the use of the standard programs.

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