Anisotropic thermal expansion in crystals of different categories

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Abstract. The three-dimensional (3D) indicatory surfaces of thermal expansion in crystals of different categories were constructed in program MathCad. Indicatory surface of thermal expansion is a sphere, spheroid, ellipsoid or surface of multiple parts, depending on the category of the crystal symmetry. The symmetry elements of thermal expansion include the symmetry elements of the point group of the crystal according Neumann's Principle.

1. Introduction
Natural and synthetic crystals are widely used in the modern instrument-making. A characteristic feature of the physical properties of single crystals is their anisotropy - different properties in different directions. We investigated the anisotropy of thermal expansion of crystals, because this property has a large practical value: different crystals are exposed thermal expansion to both at instrumental processing and at functioning in technical devices. For the evident graphic image of anisotropy of thermal expansion it is convenient to use indicatory surfaces. Radius-vector of this surface is proportional to the size of the relative lengthening of crystal in this direction at heating, [1].

The purpose of work: investigation of conformity between symmetry of surface thermal expansion and crystal symmetry.

2. Research method
Quantitatively, the thermal expansion is described by the coefficient of linear thermal expansion $\alpha_n$, which equals to the ratio of the relative change in body length along some particular direction $n$ at heating to the temperature increment:

$$\alpha_n = \frac{\Delta l/l}{\Delta T}$$  \hspace{1cm} (1)

Thermal expansion of any crystal is described by nine coefficients $\alpha_{ij}$, formative the second-order symmetric tensor.

For a definite choice of the coordinate system (the choice is determined by installation rules and associated to the elements of the symmetry of the crystal) number of independent coefficients $\alpha_{ij}$ decreases. The higher symmetry of the crystals, the smaller of coefficients describe the thermal expansion of crystal, table 1. Coefficient of thermal expansion in any direction, [2]:

$$\alpha_{ij}=\sum \alpha_{ij}n_i n_j,$$  \hspace{1cm} (2)

where:
- $\alpha_{ij}$ - coefficients of thermal expansion;
- $n_i, n_j$ - components of the vector of unit length determining an some direction in the crystal.
Table 1. The equations of indicatory surfaces of thermal expansion.

| Category of symmetry | View of the tensor of thermal expansion | The number of independent parameters | The equations of indicatory surfaces |
|----------------------|----------------------------------------|-------------------------------------|------------------------------------|
| Highest              | \[
\begin{pmatrix}
\alpha_{xx} & 0 & 0 \\
0 & \alpha_{xx} & 0 \\
0 & 0 & \alpha_{xx}
\end{pmatrix}
\] | 1 | \[\alpha_n = \alpha_{xx}\] |
| Middle               | \[
\begin{pmatrix}
\alpha_{xx} & 0 & 0 \\
0 & \alpha_{xx} & 0 \\
0 & 0 & \alpha_{zz}
\end{pmatrix}
\] | 2 | \[\alpha_n = \alpha_{xx} \cdot (n_x^2 + n_y^2) + \alpha_{zz} \cdot n_z^2\] |
| Lowest               | \[
\begin{pmatrix}
\alpha_{xx} & 0 & 0 \\
0 & \alpha_{yy} & 0 \\
0 & 0 & \alpha_{zz}
\end{pmatrix}
\] | 3 | \[\alpha_n = \alpha_{xx} \cdot n_x^2 + \alpha_{yy} \cdot n_y^2 + \alpha_{zz} \cdot n_z^2\] |
|                      | \[
\begin{pmatrix}
\alpha_{xx} & 0 & \alpha_{xz} \\
0 & \alpha_{yy} & 0 \\
\alpha_{zx} & 0 & \alpha_{zz}
\end{pmatrix}
\] | 4 | \[\alpha_n = \alpha_{xx} \cdot n_x^2 + \alpha_{yy} \cdot n_y^2 + \alpha_{zz} \cdot n_z^2 +
+ 2 \cdot \alpha_{xz} \cdot n_x \cdot n_z\] |
|                      | \[
\begin{pmatrix}
\alpha_{xx} & \alpha_{xy} & \alpha_{xz} \\
\alpha_{yx} & \alpha_{yy} & \alpha_{yz} \\
\alpha_{zx} & \alpha_{zy} & \alpha_{zz}
\end{pmatrix}
\] | 6 | \[\alpha_n = \alpha_{xx} \cdot n_x^2 + \alpha_{yy} \cdot n_y^2 + \alpha_{zz} \cdot n_z^2 +
+ 2 \cdot \alpha_{xy} \cdot n_x \cdot n_y + 2 \cdot \alpha_{xz} \cdot n_x \cdot n_z +
+ 2 \cdot \alpha_{yz} \cdot n_y \cdot n_z\] |

For the construction of 3D revolving models of indicatory surfaces would be convenient to use application package MathCad. Great mathematical capabilities of this package make it a convenient tool for physical research [3, 4].

Within this package the program was created, that allows to construct of indicatory surfaces of thermal expansion. Analysis of the received indicatory surfaces allows defining the symmetry and the anisotropy of the properties, and, if necessary, establishing the directions of its extreme value.
3. Result and discussion

3.1 Highest category
Thermal expansion of crystals of the highest category symmetry (cubic crystal system) is described by a single coefficient $\alpha_{xx}$. For any cubic crystal, indicatory surface has a form of a sphere, figure 1. Thus, the crystals of higher category evenly broaden on all directions, saving the primary form.

![Figure 1](image1.png)

**Figure 1.** The indicatory surface of thermal expansion of the cubic crystal and its projection on the plane (XOY).

3.2 Middle category
For the crystals of middle category (crystals of this category have an third, fourth or sixth order axis of rotation; the axis Z is directed along its) there are number of interesting cases:

a) all the coefficients of thermal expansion are positive, and $\alpha_{xx} < \alpha_{zz}$. For example, for crystal of zinc: $\alpha_{xx} = 14 \cdot 10^{-6}$ °C$^{-1}$, $\alpha_{zz} = 55 \cdot 10^{-6}$ °C$^{-1}$ [5], figure 2.

![Figure 2](image2.png)

**Figure 2.** The indicatory surface of thermal expansion of zink and its projection on the plane (XOY).

For the zinc the indicatory surface is elongated along the axis Z. This axis coincides with the axis of the sixth order. With a uniform heating of zinc, in this direction crystal lengthened stronger than in the perpendicular direction.

b) all the coefficients of thermal expansion are positive, and $\alpha_{zz} < \alpha_{xx}$. As, for example, for $\alpha$-quartz: $\alpha_{xx} = 14 \cdot 10^{-6}$ °C$^{-1}$, $\alpha_{zz} = 9 \cdot 10^{-6}$ °C$^{-1}$, figure 3.
Figure 3. The indicatory surface of thermal expansion of $\alpha$-quartz and its projection on the plane (XOY).

It is seen that surface of thermal expansion in this case is the spheroid, flattened along the axis of Z. This direction of minimum increase of quartz at heating. And maximally - in perpendicular direction.

c) especially highlight case when one of the coefficients of thermal expansion is less than zero. As an example, the indicatory surface of thermal expansion of calcite $\text{CaCO}_3$, which is widely used in an optical instrument production. Its coefficients of thermal expansion: $\alpha_{xx} = -5.2 \cdot 10^{-6} \degree\text{C}^{-1}$, $\alpha_{zz} = 22.6 \cdot 10^{-6} \degree\text{C}^{-1}$. The indicatory surface of thermal expansion of calcite - surface of multiple parts with positive (light) and negative (dark) areas of thermal expansion, figure 4. It is seen, that along the axis $Z$, the thermal expansion of calcite is maximal. Perpendicular to this axis is the region of negative thermal expansion (compression). Thus, at heating, calcite is lengthened in one direction, and in other is shortened. Also near the axis of $Z$ there is a cone of directions with half-angle 75°56', along which the expansion (compression) is zero. In these directions a crystal does not change at heating.

Figure 4. The indicatory surface of thermal expansion of calcite with increased fragment of the negative part and its projection on the plane (XOY).

Thus indicatory surfaces of thermal expansion of crystals middle category are spheroids. The axis of rotation is the main axis of symmetry (axis Z).
3.3 Lowest category

For crystals of the lowest category, depending on the symmetry and, accordingly, the number of independent coefficients of thermal expansion, there are also a number of cases:

a) three independent coefficients of thermal expansion for the orthorhombic crystal system, characterized by the presence of three mutually perpendicular two-order axes of symmetry.

For example, for a crystal of aragonite:

\[ \alpha_{xx} = 35 \times 10^{-6} \, ^\circ \text{C}^{-1}, \quad \alpha_{yy} = 17 \times 10^{-6} \, ^\circ \text{C}^{-1}, \quad \alpha_{zz} = 10 \times 10^{-6} \, ^\circ \text{C}^{-1} \]

The indicatory surface thermal expansion of aragonite is shown in figure 5.

![Figure 5](image)

Figure 5. The indicatory surface of thermal expansion of aragonite and its projection on the planes (XOY), (XOZ) and (ZOY).

It is seen that all the projections are ellipses. Indicatory surface of such crystals is a triaxial ellipsoid with axes coinciding with the coordinate axes, which coincide with the second order axis of symmetry.

b) in less symmetrical crystals in this category (the monoclinic crystal system) the indicatory surface is described by four thermal coefficients. For example, for a crystal of potassium tartrate:

\[ \alpha_{xx} = 12 \times 10^{-6} \, ^\circ \text{C}^{-1}, \quad \alpha_{yy} = 44.8 \times 10^{-6} \, ^\circ \text{C}^{-1}, \quad \alpha_{zz} = 32 \times 10^{-6} \, ^\circ \text{C}^{-1}, \quad \alpha_{xz} = -12 \times 10^{-6} \, ^\circ \text{C}^{-1} \]

The indicatory surface of such crystals in projection has one ellipse only - perpendicular to the axis Y, that coincides with the only axis of symmetry in these crystals, figure 6.

![Figure 6](image)

Figure 6. The indicatory surface of thermal expansion of potassium tartrate and its projection on the plane (XOZ).

4. Conclusion

The form and orientation of the indicatory surfaces of thermal expansion of the crystals is related to their symmetry according Neumann’s Principle: the symmetry elements of any physical property of a crystal must include the symmetry elements of the point group of the crystal.
As the result of investigation of anisotropy of thermal crystal expansion has been shown:

- Thermal expansion of crystals of the highest category is isotropic.
- When heated, the crystals of middle and lowest category can elongate in all directions or in some directions to shorten and elongated in other ones.
- An indicatory surface of thermal expansion of such crystals is an ellipsoid if all $\alpha_{ij}$-positive or surface with positive and negative parts, if some $\alpha_{ij}$-negative.
- In last case there are certain directions in a crystal along which thermal expansion is equal to zero.

References

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