SOME PECULIARITIES IN THE THERMAL DEFORMATION OF CRYSTALS

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Translated from Kristallografiya, Vol. 1, No. 1, pp. 95-104, January-February, 1956
Original article submitted September 20, 1955

The article shows that the thermal expansion of crystals cannot be reduced merely to a simple elongation of the crystal in all directions passing through any point in its interior. A correct pattern of the thermal expansion of crystals is given by the transformation of the unit radii of a sphere to the radius-vectors of an ellipsoid OB by means of translation vectors AB (Fig. 2). The coefficients of thermal expansion of crystals are assumed to be the intercepts AC and not the intercepts AD. The dependence of the coefficients of expansion of a crystal on direction is given by formula (8), by means of which it is possible to construct all imaginary surfaces of coefficients of expansion of crystals (Figs. 9-15). A more complete picture of the thermal deformation of crystals calls for an investigation of the surfaces of the coefficients of thermal displacement BC (Fig. 2) of crystals.

It is well known that crystals undergo *homogeneous deformation* on thermal expansion. One of its peculiarities is that a sphere, imagined to be separated somewhere inside a crystal, is transformed by the deformation into an ellipsoid, and a cube into a parallelepiped. In the homogeneous deformation of plane figures, a circle is transformed into an ellipse and a square into a parallelogram.

Such a definition of the thermal deformation of crystals allows the thermal deformation to be understood in different ways. We shall consider two treatments of this phenomenon: one definitely incorrect and the other correct; or, better, more correct, since it is amenable to further improvement. We shall commence with the first.

Incorrect Concept of the Thermal Deformation of Crystals

We assume that the thermal expansion of crystals occurs in such a manner that every radius of a sphere, imagined to be separated inside the crystal, is transformed into an identically directed radius-vector of an ellipsoid by simple elongation or compression. This means that in a plane diagram the radius of a circle OA is transformed into a radius-vector of the ellipse OB, OC into OD, OE into OF, etc. (Fig. 1).

We assume as *principal coefficients of expansion*, the magnitudes

$$\alpha_1 = \frac{AB}{OA \cdot t} = \frac{a_1 - r}{rt}, \quad \alpha_2 = \frac{DC}{OC} = \frac{a_2 - r}{rt},$$

where a_1 is the length of the principal horizontal semiaxis of the ellipse; a_2 is the length of the principal vertical semiaxis of the ellipse; r is the length of the radius of the circle; and t is the increase in temperature.

If the thermal deformation of crystals actually occurred by simple elongation of all the radii of the circle, we should have to assume as coefficient of expansion of the crystal along any oblique direction the magnitude

$$\alpha' = \frac{EF}{OE \cdot t} = \frac{R - r}{rt},$$

where R denotes the length of the variable radius-vector of the ellipse. It is not difficult to see, however, that the described mechanism of thermal de-

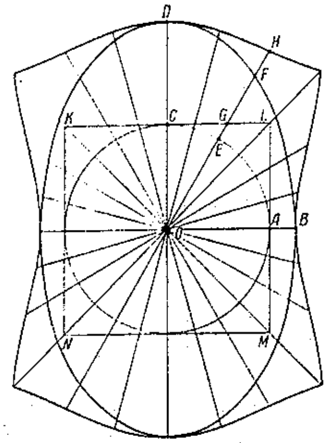

Fig. 1. If the deformation of a circle to form an ellipse occurs in such a manner that any point E on the circumference passes to the point F, the point G on the side of the square ought to pass to the point H. Accordingly, the square ought to be transformed into the curvilinear shown in the diagram.

formation of crystals, with all its simplicity and apparent clarity, is greatly in error, if not from the practical standpoint, at least from the theoretical standpoint. This becomes perfectly obvious if we apply this mechanism not to the deformation of a circle, but to that of a square KLMN. In this case, it appears that the square is not transformed into a parallelogram, but into some curvilinear figure, shown in the diagram. To construct any point H of this figure, the length of the intercept GH must be determined. If we assume that the coefficient α' has the value given above, the length of the intercept GH may easily be found from the relationship

$$\frac{GH}{OG} = \frac{R-r}{r},$$

since the length of the radius-vector OG of the square is known for each of its points G. If the crystal were deformed by thermal expansion in the manner indicated, its lattice would be distorted. This means that it could have a strictly lattice structure at only one definite temperature with which, of course, it is impossible to agree.

We have examined this incorrect treatment of homogeneous deformation in such detail because, following the footsteps of earlier authors [1], certain contemporary crystal physicists [2], including in the past the author of the present article [3], have unfortunately resorted to it.

By way of example, we shall cite one of the usual discussions based on the incorrect mechanism of homogeneous deformation which we have considered. We shall consider essentially the derivation of one of the most important formulas of crystal physics, although specifically the same thermal expansion of crystals will be borne in mind.

If we assume that the radius of a deformed circle is equal to unity, the equation of the ellipse obtained from it may be written in Cartesian coordinates, referred to the principal axes of the ellipse, as follows:

$$\frac{x_1^2}{(1+\alpha_1)^2} + \frac{x_2^2}{(1+\alpha_2)^2} = 1.$$

Making use of the substitutions

$$x_1 = R\cos(RX_1) = (1+\alpha')\,c_1,$$
$$x_2 = R\cos(RX_2) = (1+\alpha')\,c_2$$

and ignoring squares and derivatives of the small quantities α', α_1, α_2, we reduce the equation of the ellipse to the form

$$\alpha' = \alpha_1 c_1^2 + \alpha_2 c_2^2.$$

We have obtained this formula bearing in mind the deformation of plane figures. If we repeated our argument as applied to three-dimensional figures, we should arrive at the formula

$$\alpha' = \alpha_1 c_1^2 + \alpha_2 c_2^2 + \alpha_3 c_3^2, \qquad (1)$$

enabling us to calculate the coefficient of expansion α' from the three known principle coefficients α_1, α_2, α_3 for any direction in the crystal defined by the direction cosines c_1, c_2, c_3.

More Correct Concept of the Thermal Expansion of Crystals

This concept is based on the assumption that the thermal deformation of a crystal may be described by the system of equations

$$\left.\begin{aligned} x_1' &= a_1 x_1 \\ x_2' &= a_2 x_2 \\ x_3' &= a_3 x_3 \end{aligned}\right\}, \qquad (2)$$

where x_1, x_2, x_3 are the Cartesian coordinates of any point of the crystal before deformation, x_1', x_2', x_3' are the coordinates of the same point after deformation, and a_1, a_2, a_3 are some constants (positive or negative real numbers). It is assumed that the coordinates are referred to the system of the principal axes of the crystal which theoretically may always be found (for monoclinic and triclinic crystals, the position of the principal axes is fixed only for a given temperature). If it is a question of the deformation of a sphere which we imagine to be separated inside the crystal, or actually ground out of it, we take the center of the sphere as the origin of the coordinates.

We assume that all the points of interest to us are arranged after deformation on the surface of this sphere and that the radius of the latter is equal to unity. This means that the coordinates x_1, x_2, x_3 are connected together by the equation

$$x_1^2 + x_2^2 + x_3^2 = 1. \tag{3}$$

Having determined from equation (2) the coordinates x_1, x_2, x_3 and substituting the values found for them in the equation (3) for the sphere, we obtain the expression

$$\frac{x_1'^2}{a_1^2} + \frac{x_2'^2}{a_2^2} + \frac{x_3'^2}{a_3^2} = 1, \tag{4}$$

which represents the equation of an ellipsoid. We have shown that the sphere is transformed by equations (2) into an ellipsoid. Similarly, it may be shown that a cube is converted by them into a parallelepiped. For this purpose, it is necessary to take as starting equation not that of a sphere, but the equation for two parallel sides of a cube, and to show that by means of equations (2) it is transformed into the equations of two planes equidistant from the origin of the coordinates and parallel to each other.

As is known, the equation of a plane may be represented in the form

$$\frac{x_1}{A_1} + \frac{x_2}{A_2} + \frac{x_3}{A_3} = 1,$$

where A_1, A_2, A_3 are the lengths of the intercepts of the plane with the coordinate axes. If this equation is taken as the equation for one face of a cube, the cube face parallel to it will have the equation

$$\frac{x_1}{-A_1} + \frac{x_2}{-A_2} + \frac{x_3}{-A_3} = 1.$$

Substituting in both these equations the values of x_1, x_2, x_3 found from equations (2), we get

$$\frac{x_1'}{a_1A_1} + \frac{x_2'}{a_2A_2} + \frac{x_3'}{a_3A_3} = 1,$$

$$\frac{x_1'}{-a_1A_1} + \frac{x_2'}{-a_2A_2} + \frac{x_3'}{-a_3A_3} = 1.$$

These are the equations for two parallel planes equidistant from the origin of the coordinates, which was to be demonstrated.

We shall examine the process of thermal deformation, described by equations (2) in greater detail with reference to the plane scheme (Fig. 2). We shall take a circle having a radius equal to unity. We divide it into 4n equal parts (24 parts in the diagram). We connect the points of division to the center of the circle; we have a system of radii of the circle before its transformation into an ellipse. We now apply to each point of division of the circle, and correspondingly to each radius of the latter, the transformation (2), assuming $x_3 = 0$. We take first the point K with the coordinates $x_1 = 1$, $x_2 = 0$. Multiplying them respectively by a_1 and a_2, we get $x_1' = a_1$, $x_2' = 0$. This result shows that the point K, after deformation while remaining on the X_1 axis, ought to be displaced to the right if $a_1 > 1$, or to the left, if $a_1 < 1$. In constructing the diagram we assumed $a_1 = 1.25$, $a_2 = 2.00$. In accordance with this, our point was displaced to the position E on the right of K. It follows from the foregoing that $a_1 = OE$. Similarly, it may be shown that $a_2 = OF$. As will be seen, the constants a_1, a_2, from the geometrical point of view, are the semiaxes of the ellipse into which the circle is transformed as the result of deformation. If we apply our transformation to the point A, we find that, after deformation, it will have moved to the point B along the **displacement vector** AB. In accordance with

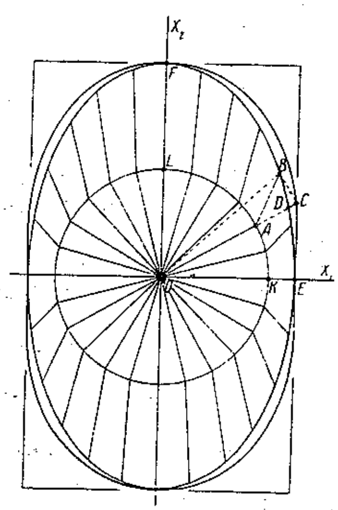

Fig. 2. Transformation of a circle into an ellipse as described by equations (2) and corresponding exactly to the observed thermal deformation of crystals. In this case, the vector OA is transformed into the vector OB by means of the displacement vector AB, which transfers the point A to B. In this case, a magnitude proportional to the length of the intercept AC is taken as coefficient of expansion in the OA direction.

this, the radius of the circle OA is transformed into the radius vector OB of the ellipse. If we complete this construction for all the points of division of the circle, without representing for the sake of simplicity the radius vectors of the ellipse, we obtain the complete deformation pattern shown in Fig. 2. It will be seen that this pattern differs substantially from that previously considered (Fig. 1).

By using formulas (2), it is easy to calculate and construct the diagram for the transformation of a square into a parallelogram (Fig. 3).

Returning to Fig. 2, there is to be seen in it the point D, coinciding with the point of intersection of the ellipse and the prolonged straight line OA, and the point C, which is located at the intersection of the same straight line with the normal BC dropped from the point B onto this straight line. We transfer these and other points of the diagram considered to a special diagram (Fig. 4). We denote the angles formed by the straight line OC with the axes of the coordinates by φ_1, φ_2, and their cosines, which are the direction cosines of this straight line, by c_1, c_2. It is evident that the coordinates of the point A for OA = 1 are c_1, c_2 and the coordinates of point B, in agreement with formulas (2) are equal to a_1c_1; a_2c_2. We furthermore denote the length of the intercept of the straight line OC by a'.

The diagram shows that the normal equation of the straight line GH for this notation may be written in the form

$$a' = x_1c_1 + x_2c_2.$$

Since this straight line passes through the point B, the equation cited will not be violated if, instead of x_1, x_2 we substitute the coordinates of these points a_1c_1; a_2c_2. After this substitution, the equation cited becomes the equation

$$a' = a_1c_1^2 + a_2c_2^2. \tag{5}$$

We must here digress slightly from the main theme of our article and point out that if, in the equation (5) we have obtained, the quantities a_1, a_2 are regarded as constants and the quantities a', c_1, c_2 as variables, taking into account, of course, the fact that the sum of the squares of the direction cosines is always equal to unity,

$$1 = c_1^2 + c_2^2, \tag{6}$$

this equation (5) will define in Cartesian coordinates some curve which, after due examination, is found to be an oval-like curve, with four points in common with the ellipse under consideration (Fig. 2), and situated outside the latter with all its other points.

We return to our subject. We subtract equation (6) from (5)

$$a' - 1 = (a_1 - 1)\,c_1^2 + (a_2 - 1)\,c_2^2.$$

As we already know, the quantities $a_1 - 1$ and $a_2 - 1$ represent the principal coefficients of expansion α_1 and α_2. If, in agreement with this, we denote the quantity $a' - 1$ by α', the last-mentioned equation becomes

$$\alpha' = \alpha_1c_1^2 + \alpha_2c_2^2. \tag{7}$$

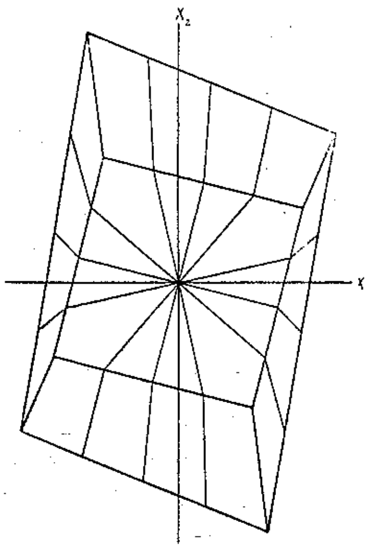

Fig. 3. Diagram to show that a square is transformed into an oblique parallelogram by equations (2).

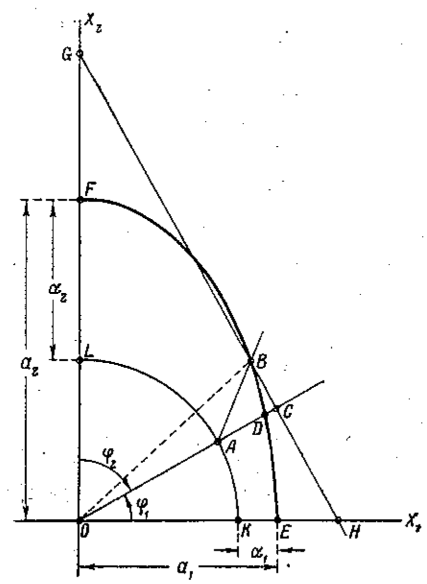

Fig. 4. Diagram for deduction of Eq. (8).

Formula (7) describes the thermal expansion of plane figures. If we repeated our considerations, having in mind three-dimensional figures, we should obtain the equation

$$\alpha' = \alpha_1 c_1^2 + \alpha_2 c_2^2 + \alpha_3 c_3^2. \qquad (8)$$

We now direct our attention to the fact that formulas (1) and (8) do not differ from each other in outline, despite the fact that the first of them is approximate (since, in deriving it we ignored squares and derivatives of the quantities α', $\alpha_1, \alpha_2, \alpha_3$) and the second is perfectly accurate. This is due to the fact that in formula (1), by the quantity α' we understood the intercept AD (see Fig. 4), which is actually defined approximately by this formula, whereas, in formula (8) by the quantity α' we understood the intercept AC, which is defined perfectly accurately by this formula.

Taking this into account, and bearing in mind the fact that formula (8) has been derived on the basis of more exact concepts of thermal deformation, we shall henceforth understand by the coefficient of expansion α' a quantity proportional to the intercept AC and not the intercept AD.

At first sight, such a definition of the coefficient of expansion – in fact not novel – may appear to be too artificial, since the point C is situated outside the ellipse (i.e., outside the crystal, if before deformation it is given the shape of a sphere). It is necessary, however, to take into consideration the fact that the real transformation of the vector OA (Figs. 2 and 4) into the vector OB by means of the *displacement vector* AB occurs not only by *extension* of the vector OA to the magnitude of the intercept AC, but also on account of the *shift* CB, as the result of which the point C coincides with the point B, where it ought to be.

It is very important to note that the formula (8) we have derived, being an equation of second degree with regard to the variables c_1, c_2, c_3, is an equation of fourth degree with regard to the variables x_1, x_2, x_3. This may easily be verified by replacing the variables c_1, c_2, c_3, α' by their equivalent quantities

$$\frac{x_1}{\alpha'}, \ \frac{x_2}{\alpha'}, \ \frac{x_3}{\alpha'}, \ \sqrt{x_1^2 + x_2^2 + x_3^2}.$$

It follows from this that equation (8), despite often-encountered statements, cannot express in *Cartesian coordinates* any surface of a second order, in particular the surface of an ellipsoid.

The fact that in individual cases equation (8) cannot express an ellipsoid *even approximately* is clear from the following. We know that the coefficient of calcite along the principal axis has a positive sign, and along directions perpendicular thereto a negative sign. This means that in certain oblique directions the coefficient of expansion ought to be exactly equal to zero, i.e., certain radius vectors of the ellipsoid ought also to be equal to zero. Such ellipsoids do not exist.

We should here like to point out that, despite the previously often-repeated view [4,5], in the thermal expansion of calcite there is not only no contradiction of the ellipsoid law, but, on the contrary, a most elegant confirmation of this law, since, in this case also, the sphere is transformed by equations (2) into an ellipsoid and a circle into an ellipse (Fig. 5).

Form, Symmetry, and Antisymmetry of Surfaces of the Coefficients of Expansion of Crystals

By means of equation (8), it is possible to find from the three known principal coefficients of expansion $\alpha_1, \alpha_2, \alpha_3$, the coefficient of expansion α' for any direction in the crystal, determined by the cosines c_1, c_2, c_3, which affords the possibility, by plotting from one point in different directions radius vectors proportional to α', to construct theoretically all conceivable forms of *surfaces of coefficients of expansion* of crystals for α_1, α_2, α_3 differing from each other in magnitude and sign.

For crystals of the cubic system, all three principal coefficients of expansion are equal to each other and all three are positive ($\alpha_1 = \alpha_2 = \alpha_3 > 0$). In this case, equation (8) assumes the form

$$\alpha' = \alpha_1 (c_1^2 + c_2^2 + c_3^2) = \alpha_1. \qquad (9)$$

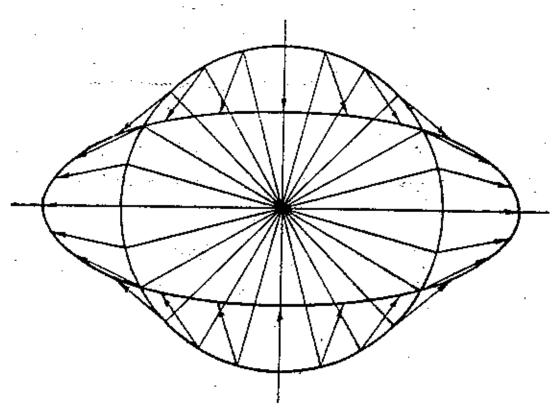

Fig. 5. Diagram showing that the ellipsoid law for thermal deformation remains valid even if one of the principal coefficients has a negative sign.

The corresponding surface evidently is a sphere with positive radii, a white sphere having the symmetry $\infty/\infty \cdot m$.

For $\alpha_3 \neq \alpha_2 = \alpha_1$; $\alpha_1, \alpha_3 > 0$, the surface of the coefficients of expansion, expressed by the equation

$$\alpha' = \alpha_1 (c_1^2 + c_2^2) + \alpha_3 c_3^2, \qquad (10)$$

becomes an oval-like, positive (white) surface of revolution, prolate (for $\alpha_3 > \alpha_1$), or oblate (for $\alpha_3 < \alpha_1$) along the X_3 axis (Figs. 6 and 7), and, in both cases having the symmetry $m \cdot \infty : m$. Such surfaces describe the simplest and most frequently encountered case of the thermal expansion of optically uniaxial crystals.

It was pointed out in the foregoing that, in calcite, α_3 has a positive sign and α_1 a negative sign. In accordance with this, equation (8) for this and similar uniaxial crystals will have the form

$$\alpha' = -\alpha_1(c_1^2 + c_2^2) + \alpha_3 c_3^2. \qquad (11)$$

Figure 8 shows the corresponding surface of revolution having the symmetry $m \cdot \infty : m$. As will be seen, it consists of two ovoid positive (white) regions and one toroidal negative (black) region.

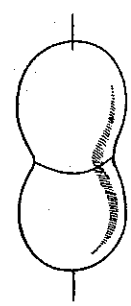

Fig. 6. Surface of coefficients of expansion of crystals satisfying the equation $\alpha' = \alpha_1(c_1^2 + c_2^2) + \alpha_3 c_3^2$ for $\alpha_3 > \alpha_1$.

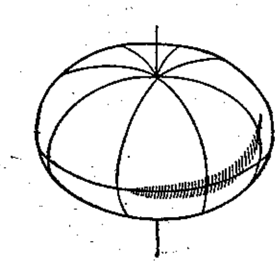

Fig. 7. Surface satisfying the equation $\alpha' = \alpha_1(c_1^2 + c_2^2) + \alpha_3 c_3^2$ for $\alpha_3 < \alpha_1$.

If all the principal coefficients of expansion are positive and all differ from each other ($\alpha_1 \neq \alpha_2 \neq \alpha_3$; $\alpha_1, \alpha_2, \alpha_3 > 0$), equation (8) assumes the form

$$\alpha' = \alpha_1 c_1^2 + \alpha_2 c_2^2 + \alpha_3 c_3^2. \qquad (12)$$

The corresponding surface having the $m \cdot 2 : m$ symmetry is shown in Fig. 9. It describes the most frequently encountered cases of the thermal expansion of the majority of optically biaxial crystals.

If one of the principal coefficients, say α_3, has a negative sign, equation (8) becomes

$$\alpha' = \alpha_1 c_1^2 + \alpha_2 c_2^2 - \alpha_3 c_3^2. \qquad (13)$$

The corresponding surface (Fig. 10) consists of two negative (black) ovoid regions, and one elongated

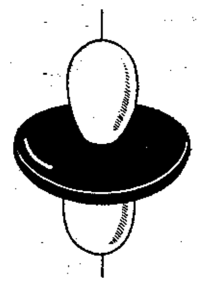

Fig. 8. Surface satisfying the equation $\alpha' = -\alpha_1(c_1^2 + c_2^2)\alpha_3 c_3^2$.

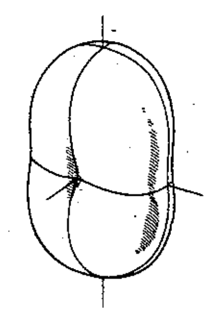

Fig. 9. Surface satisfying the equation $\alpha' = \alpha_1 c_1^2 + \alpha_2 c_2^2 + \alpha_3 c_3^2$.

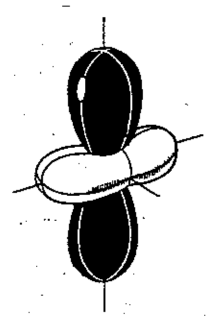

Fig. 10. Surface satisfying the equation $\alpha' = \alpha_1 c_1^2 + \alpha_2 c_2^2 - \alpha_3 c_3^2$.

positive (white) region, having the form of an elongated annulus (bread roll). Theoretically, it may be predicted that such surfaces, having the symmetry m · 2 : m, may describe the thermal expansion of some biaxial crystals.

The surfaces described change their form substantially when one or two of the principal coefficients of expansion become equal to zero.

For $\alpha_1 = 0$, equation (10) becomes

$$\alpha' = \alpha_3 c_3^2. \tag{14}$$

The corresponding surface of revolution, shown in Fig. 11, has the symmetry m · ∞ : m and represents a pair of ovoid (white) regions, osculating at one point.

The same equation (10) for $\alpha_3 = 0$ assumes the form

$$\alpha' = \alpha_1 (c_1^2 + c_2^2). \tag{15}$$

The corresponding surface of revolution, shown in Fig. 12, has the form of a round bread roll (white) with two funnel-shaped depressions osculating at their apices. The surface has the symmetry m · ∞ : m.

If one of the principal coefficients in equation (12) is equated to zero, then (for $\alpha_3 = 0$), it assumes the form

$$\alpha' = \alpha_1 c_1^2 + \alpha_2 c_2^2. \tag{16}$$

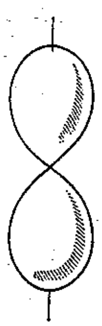

Fig. 11. Surface satisfying the equation $\alpha' = \alpha_3 c_3^2$.

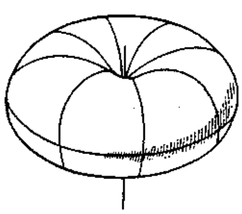

Fig. 12. Surface satisfying the equation $\alpha' = \alpha_1(c_1^2 + c_2^2)$.

The corresponding surface, shown in Fig. 13, has the form of an elongated bread roll with two funnel-shaped depressions, osculating at their apices. The surface has the symmetry m · 2 : m.

It remains to consider surfaces in which, for equality to zero of one coefficient, the other two have different signs. If, in equation (13), we put $\alpha_3 = 0$ and change the sign of c_1, it becomes

$$\alpha' = -\alpha_1 c_1^2 + \alpha_2 c_2^2. \tag{17}$$

The corresponding surface, shown in Fig. 14, represents a pair of identical negative (black), and a pair of identical, but of another size, positive (white) ovoid regions, connected by their apices at one point. The surface has the symmetry m · 2 : m.

If, in the last-mentioned equation, the principal coefficients of expansion are antiequal to each other, it assumes the form

$$\alpha' = \alpha_1 (c_2^2 - c_1^2). \tag{18}$$

The corresponding surface, shown in Fig. 15, a pair of identical white ovoid regions and a pair of black ovoid regions, antiequal to the former, connected together by their apices at one point. The surface has the symmetry m · 2 : m, and it also has the property of antisymmetry (m · 4 : m).

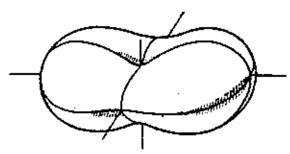

Fig. 13. Surface satisfying the equation $\alpha' = \alpha_1 c_1^2 + \alpha_2 c_2^2$.

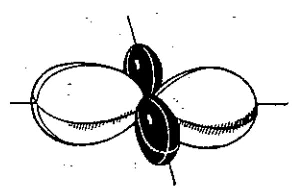

Fig. 14. Surface satisfying the equation $\alpha' = -\alpha_1 c_1^2 + \alpha_2 c_2^2$.

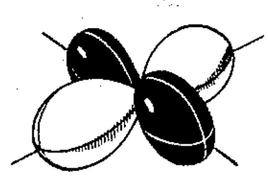

Fig. 15. Surface satisfying the equation $\alpha' = \alpha_1(c_2^2 - c_1^2)$.

We consider the last five surfaces (Figs. 11-15) constructed theoretically on the assumption that one or two principal coefficients of expansion are equal to zero, to be unreal for crystals, but assume that it will be possible artificially to produce uniform anisotropic materials, the thermal deformation of which will correspond to these surfaces.

In conclusion, we would point out that the pattern of thermal deformation of crystals we have outlined is not final, since we have restricted ourselves merely to the investigation of the surfaces of the coefficients of thermal expansion and have left entirely out of consideration the surfaces of the coefficients of thermal shear of crystals. We propose to deal with this second problem in a future article.

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