TEMPERATURE DEPENDENCE OF THERMAL EXPANSION COEFFICIENT OF CRYSTALS WITH CUBIC SYNGONY

A. P. Nasekovskii


A simple analytic temperature relationship for the thermal expansion coefficient of crystals with cubic syngony was obtained, and the thermal expansion coefficients of some crystals of this class were determined experimentally; the results agreed satisfactorily with the curve obtained from formulas (5) and (6). The temperature range from liquid nitrogen up to temperatures around 1000° K was investigated, and the results were compared with data given by other authors.

Determination of the temperature dependence of thermal expansion coefficient for crystals provides substantial information on structure, bonds between particles, phase transformations, and a number of other facts about crystal processes. With the necessary degree of accuracy and sensitivity in the measurements a fairly complex relationship is found between thermal expansion coefficient and temperature. We were set the task of obtaining an analytic expression for the thermal expansion coefficient of crystals with cubic syngony and verifying it experimentally.

The law of linear thermal expansion of isotropic crystals is characterized by the following formula:

\[ l_T = l_{T_0} \exp \left( \frac{1}{\alpha} \int a(T) dT, \right) \]  \hspace{1cm} (1)

where \( l_T \) is the length of the specimen at temperature \( T \); \( l_{T_0} \) is the length of the same specimen at the beginning of the selected temperature range; and \( \alpha \) is the linear thermal expansion coefficient of the solid.

The Grüneisen relation [1] makes it possible to relate the thermal expansion coefficient to the temperature in terms of the heat capacity at constant volume and high temperature, but at low temperatures the Grüneisen constant varies with the temperature.

A more general expression for the thermal expansion coefficient, suitable for use in the temperature range from 0° K to temperatures close to the melting point of the solid, is the formula

\[ \alpha = \gamma \frac{C_V \alpha}{3V} + \left( \frac{\partial \gamma}{\partial T} \right)_V \frac{E_v \alpha}{3V}, \]  \hspace{1cm} (2)

where \( \gamma \) is the Grüneisen constant; \( C_V \) is the heat capacity at constant volume; \( \gamma \) is the isothermal compressibility; \( E_v \) is the vibrational part of the lattice energy; and \( V \) is the volume of the solid.

With the relationship for temperature dependence of heat capacity of cubic crystals obtained in [3] and Eq. (2) a clear relationship between the thermal expansion coefficient and temperature can be obtained. According to [3] the expression for heat capacity has the following form:

\[ C_V = \frac{3R(T/\Theta)^3}{(T/\Theta + 1)^3}. \]  \hspace{1cm} (3)

Here \( R \) is the universal gas constant, and \( \Theta \) is a temperature comprising one third of the Debye temperature, while the vibrational part of the lattice energy is

\[ E_v = \frac{24RT}{(T/\Theta + 1)^3}. \]  \hspace{1cm} (4)

Thus from Eqs. (2), (3), and (4) we obtain

\[ \alpha = \frac{xR(T/\Theta)^3}{V} \left[ \frac{C_v}{(T/\Theta + 1)^3} + \left( \frac{\partial \gamma}{\partial T} \right)_V \frac{E_v}{(2T/\Theta + 1)^3} \right]. \]  \hspace{1cm} (5)

As shown by experience, at high temperatures \( \frac{\partial \gamma}{\partial T} = 0 \), and Eq. (5) takes on a simpler form:

\[ \alpha = \frac{xR(T/\Theta)^3}{V} \left( \frac{C_v}{(T/\Theta + 1)^3} + \frac{E_v}{(2T/\Theta + 1)^3} \right). \]  \hspace{1cm} (6)

In order to select samples with reversible thermal expansion and also with the aim of verifying Eqs. (5) and (6) experimentally the thermal expansion coefficients of a number of crystals with cubic syngony were measured on a dilatometer, with a volume measuring device [4], capable of giving the required degree of accuracy at temperatures from the boiling point of liquid nitrogen to 1000°–1200° K. Subjects selected for investigation were materials in which phase transformations had not been postulated and which had sufficiently high chemical stability.

The low-temperature measurements were made at the boiling points of nitrogen (77.35° K) and oxygen (90.19° K), at the equilibrium temperature of a mixture of carbon dioxide with equal parts of carbon tetra-
chloride and chloroform (193°), at the equilibrium


temperature of a mixture of three parts crushed ice

with four parts of calcium chloride (225° K), at the
equilibrium temperature of two parts crushed ice and

one part common salt (255° K), and at the temperature

of melting ice (273° K). Other temperatures were se-

clected at 50-degree intervals since these intervals
gave an error no greater than the error of the length
measurements. At room temperature and tempera-
tures up to 1000° K the measurements were carried
out in special thermostated apparatus [5, 6], giving an
accuracy of not less than 0.01°, and the temperatures
were determined with the same accuracy.

Figure 1 shows the experimental temperature-depen-
dence curve for the thermal expansion coefficient
of electrolytic copper (curve 2) taken from five series
of measurements in the 77°-980° K range. This curve
was obtained by the author with the volume dilatometer
already mentioned [4]. The thermal expansion coeffi-
cient, α, was calculated directly from the experimen-
tal results. Samples of polycrystalline copper were
machined into 4 x 50 mm cylinders and annealed from
temperatures near the melting point of copper. As
seen from Fig. 1 the thermal expansion coefficient
increases rapidly with temperature between 77° and
200° K. It practically reaches its final value at this
stage; its rate of increase then falls markedly, and it
remains almost unchanged in value up to 500° K. Only
at temperatures above 500° K is there again a slow in-
crease in thermal expansion coefficient, and this con-
tinues right up to 1000° K without further deviations.
A curve for the average results from several authors
[7-9] is given in the same figure. From 77° to 450° K
these results differ little from our results. From 77°
to 250° K curve 1 deviates slightly, but systematically,
what higher than our experimental results (curve 2),
and they all intersect at 350° K. There are no data in
the literature on the temperature dependence of the
thermal expansion coefficient for germanium above
350° K.

As with copper the experimental curves 1 and 2 are
smooth over the whole temperature range investigated.
Comparison of curves 1 and 2 with the calculated curve
3 show satisfactory correspondence between the ex-
perimental and theoretical results, which shows that
the thermal expansion coefficient of germanium up to
750° K can be calculated from Eqs. (5) and (6); however
this is not to say that these equations are not suitable
at temperatures above 750° K since measurements
were not made above this temperature.

Similar investigations were also carried out with
specimens of semiconductor-purity silicon (Fig. 3).
In this case negative variation of thermal expansion
coefficient is clearly seen at temperatures below 120°
K, although the absolute value is not greater than 0.2 x
x 10⁻⁸ deg⁻¹ at 93° K.

Up to temperatures around 450° K the temperature
dependence was almost linear; above this temperature
there was little variation with temperature, and this
was also nearly linear.