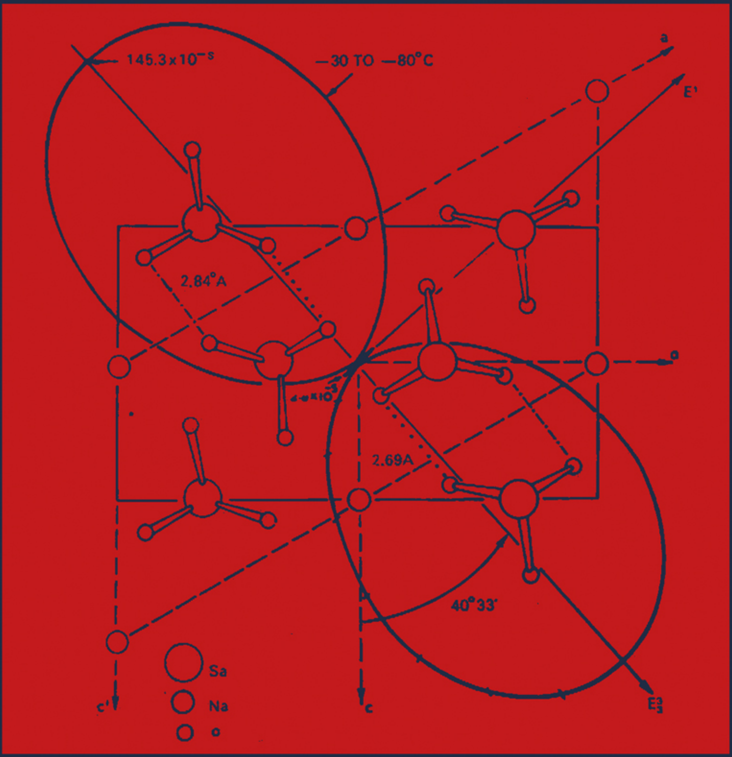
R.S.Krishnan R.Srinivasan S.Devanarayanan

THERMAL EXPANSION OF CRYSTALS



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THERMAL EXPANSION OF CRYSTALS

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PERGAMON PRESS
OXFORD · NEW YORK · TORONTO
SYDNEY · PARIS · FRANKFURT

Pergamon Press Ltd., Headington Hill Hall, Oxford
OX3 0BW, England

Pergamon Press Inc., Maxwell House, Fairview Park,
Elmsford, New York 10523, U.S.A.
Pergamon of Canada, Suite 104, 150 Consumers Road,
Willowdale, Ontario M2J IP9, Canada
Pergamon Press (Aust.) Pty. Ltd., PO Box 544. Potts Point,
N.S.W. 2011, Australia
Pergamon Press SARL, 24 rue des Ecoles,
75240 Paris, Cedex 05, France
Pergamon Press GmbH, 6242 Kronberg-Taunus,
Pferdstrasse 1, West Germany

First Edition 1979

British Library Cataloguing in Publication Data
Krishnan, R S
Thermal expansion of crystals.—(International series in the science of the solid state; vol. 12).
1. Crystals—Thermal properties 2. Expansion (Heat)
I. Title II. Srinivasan, R III. Devanarayanan, S
IV. Series
548'.5 QD937 77-30620
ISBN 0-08-021405-3

Photoset and printed at Thomson Press (India) Limited, New Delhi, India

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Preface

Thermal expansion of a solid is a direct consequence of the anharmonicity of lattice vibrations. It, therefore, provides a convenient measure of the anharmonic parameters in a crystal. The anisotropy of thermal expansion is clearly exhibited if measurements are made on a single crystal. The anisotropy is related to the crystal system.

One meets with a variety of behaviour if the thermal expansion of crystals is studied over a wide temperature range. There are crystals like germanium in which the expansion changes sign twice as the temperature is reduced. There are anisotropic crystals like calcite in which the expansion is positive in one direction and negative in the other.

The simple theory of thermal expansion of crystals given by Grüneisen in 1929 predicted the expansion co-efficient to decrease to zero as the temperature tends to the absolute zero. The expansion coefficient of many crystals near the boiling point of liquid helium is of the order of $10^{-8}/°K$. This necessitates new and sensitive experimental techniques to determine the thermal expansion in this temperature range. It was also realised that one should make measurements at low temperatures to detect deviations from the simple Grüneisen theory, arising from the complicated phonon spectrum of the lattice.

In the years from 1960 onwards there has been a spate of work on the thermal expansion of crystals—both theoretical and experimental. On the experimental side, besides the refinements in the existing techniques for lattice and macroscopic expansion measurements, several new sensitive techniques were developed to measure changes as small as 10^{-8} cm in the length of the specimen. Among these techniques mention should be made of the three-terminal capacitance dilatometer, the differential transformer dilatometer and the Fabry-Perot interference dilatometer. Though these and other techniques are described in individual papers in the literature there has been no discussion of the relative merits of these techniques. There has also been a lot of effort at automatic and continuous recording of the dilatation of a specimen as the temperature is changed. A detailed review of the different experimental techniques with a discussion of the inherent sources of error and methods for their elimination will be of interest to the experimental research worker in this field.

Considerable amount of data on thermal expansion has been collected down to 4.2 K on simple crystals by the painstaking application of one or the other experimental technique mentioned above. These results reveal the possibility of more than one contribution to the thermal expansion of a crystal. These different contributions have different origins and hence different characteristic temperature dependences at low temperatures. For example, the electronic contribution in metals at low temperatures varies linearly with the Absolute temperature and provides information on the volume derivative of the density of states at the Fermi level. The lattice contribution, on the other hand, is proportional to T^3 at low temperatures; and it is related to the pressure derivatives of the second-order elastic constants in these materials. As long as the temperature T is less than half the Debye temperature, one could use the quasi-harmonic approximation in the theory of thermal expansion. Detailed calculations on rare gas solids, cubic metals, semiconductors and ionic crystals with simple structures have been made and we have now a fair degree of understanding of the temperature variation of linear thermal expansion coefficient in these materials. However, there is a paucity of theoretical work in anisotropic materials. Some ground rules exist for a general explanation of the temperature variation of thermal expansion in these crystals. But we have as yet no sound knowledge of the crystal potential in these materials.

The measurements of thermal expansion at high temperatures almost upto the melting point of some of the cubic materials have provided information on the relative importance of cubic and quartic anharmonic terms which have been omitted in the quasi-harmonic approximation.

Precise measurements of thermal expansion at very low temperatures provide additional data for the $T = 0$ molar volume (or, lattice parameter) of a substance. This quantity enables interpretation of the van Alphen-de Haas measurements on the substance.

The thermal expansion of a crystal also shows some interesting variations when the crystal undergoes phase transformations. The phase transformation in ammonium halides have been studied with a view to testing the Ehrenfest-Pippard relations. In the case of ferroelectric crystals containing hydrogen bonds, the changes in the thermal expansion coefficients at the ferroelectric transition point are related to the reorientation of the hydrogen bonds.

This book presents a comprehensive review on these various aspects of thermal expansion. A comparison of the various methods of measurement is made with comments on the relative merits of the different methods. A very detailed review of the theory of thermal expansion is provided with critical comments on the works of various authors. The behaviour of thermal expansion when phase transformations occur, and in ferroelectric materials forms the subject matter of a separate chapter. It is hoped that this review will prove to be of value to the experimental and theoretical workers in this field.

It was also thought desirable to collect all the published data on thermal expansion of about 370 scientifically and technologically important materials (mostly crystals) and to present them for ready reference in the form of tables. The data have been fitted to empirical formulae and the constants in the formulae have been tabulated at high and at low temperatures. These tables can be used with ease.

The value of the book lies also in the comprehensive literature survey that has been done on thermal expansion of solids in general and work related to it which may prove useful for further study. There are more than 1800 references cited at the end of the book, giving the names of authors, journals and titles of papers as appeared in the literature. These references have been brought upto date till the middle of 1977. It is noteworthy that more than 74% of the publications belong to the period from 1960 to 1977. The authors hope that the comprehensive survey of the literature on thermal expansion of solids in general and work related to it presented in this book may prove useful to research workers for further study.

The authors are indebted to Dr. S.V. Subramanyam, Department of Physics, Indian Institute of Science, Bangalore, for his invaluable help in the preparation and checking the correctness of the bibliography listed in the book.

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Dated: 1.7.1977

Note added in proof:

The list of electronic materials and the pages on which their thermal expansion data are given are summarized in Appendix II.

The bibliography of papers published on the subject has been brought up to the end of February 1979 and is given under the heading "Recent References" on page 289. The total number now exceeds 2110.

31.5.79. R.S. Krishnan

CHAPTER 1

General Introduction

1.1. INTRODUCTION

The expansion of a crystal when it is heated is a direct manifestation of the anharmonic nature of the interatomic forces in solids. If the forces were purely harmonic the mean positions of the atoms would not change even though the atoms would vibrate with larger and larger amplitudes as the temperature increases. While the temperature variation of the specific heat of solids was quite well understood with the development of the Born-von Karman's theory of lattice vibrations in crystals, there was little attempt to calculate the thermal expansion of crystals in any detail till recently. This was partly because of the paucity of experimental data on the thermal expansion of crystals below room temperature. While Grüneisen's theory of thermal expansion provided a general explanation of the phenomenon on the quasi-harmonic approximation, a detailed study of the temperature variation of thermal expansion below room temperature was started only after the work of Barron (64) in 1955. The theoretical study provided an impetus to the development of refined experimental techniques to measure the thermal expansion of crystals down to liquid helium temperature. The techniques so developed are sensitive enough to measure a change in length of the specimen of a fraction of an Ångström! A large body of reliable data has been accumulated on a variety of simple crystals in which the forces of interaction are fairly well understood. A fairly satisfactory explanation has been provided for the temperature variation of the thermal expansion in these simple solids on the quasi-harmonic theory. This review deals with the progress achieved both in the theoretical and experimental study of thermal expansion in recent times. An exhaustive collection of the data on the thermal expansion of a large variety of crystals has also been made so that the work can be used as a ready reference book.

The *linear thermal expansion coefficient* α of a solid is defined as the increase in length suffered by unit length of the solid when its temperature is raised by a degree Celsius. The limiting value of the ratio $\frac{1}{l_T} \cdot \frac{\delta l}{\delta T}$ as the increase in temperature $\delta T \rightarrow 0$ is defined as the true expansion coefficient of the solid. Usually it is the mean coefficient of expansion over a temperature range δT that is measured. The smaller this range of temperature the more nearly does the mean coefficient of expansion approach the true coefficient. A similar definition holds for the volume expansion coefficient, β, of the solid. The volume expansion coefficient of the solid is related to its linear expansion coefficient. To a first degree of approximation the volume expansion coefficient is the *sum* of the linear expansion coefficients in three mutually perpendicular directions in the solid.

Solids can be crystalline or amorphous—an example for the latter being glass. We are concerned only with crystalline solids. These are available in two forms: single crystals formed by the monotonous repetition in space of a simple structural unit according to definite laws of symmetry; or polycrystalline material composed of small crystallites oriented in all possible directions. It is needless to emphasize that for any theory of the solid state a study of single crystals is of great importance. Polycrystalline material introduces great complexities in the understanding of the physical processes involved. As an example, mention may be made of cadmium and zinc where a study of the expansion of polycrystalline material yielded widely divergent results. This confusion was cleared up when single crystals of these substances were studied.

The measurement of thermal expansion of crystals is of importance for the following reasons:

1. The expansion of a crystal is intimately related to the normal modes of vibration of the crystal lattice and hence a study of it might be expected to throw some light on the nature of binding between the different units in the lattice.

2. The expansion coefficient is a structure sensitive property and reflects any transitions in crystal structure.

3. Expansion coefficient values are needed to convert the C_p values observed in experiments to the C_v values required by the theory of specific heat. The thermodynamic relation connecting them is given by

$$C_p - C_v = \beta^2 V T / \chi J \qquad (1.1.)$$

where C_p = Molar specific heat at constant pressure of the solid in Cals/°K,
C_v = Molar specific heat at constant volume of the solid in Cals/°K,
β = the volume expansion coefficient of the solid,
V = the volume of the solid,

χ = Compressibility of the solid,
T = Temperature of the solid,
and J = Mechanical equivalent of heat.

4. Precise measurements of thermal expansion at very low temperatures provide additional data for T = 0 molar volume of a substance. A knowledge of this quantity is essential to interpret properly the van Alphen-de Haas measurements on the substance.
5. Knowledge of thermal expansion at low temperatures is useful to isolate the electronic and the nuclear hyperfine contributions to the Grüneisen parameter from the lattice contribution.
6. An extremely useful quantity in physics at high pressures is the *Grüneisen parameter*. Through this parameter maximum information may be extracted from limited data, which is of advantage in experimentally difficult conditions where data are often unobtainable. Thermal expansion data enable evaluation of the Grüneisen parameter.
7. Another quantity of interest in recent years is the *second Grüneisen constant*, q, which is the first order volume derivative of the normal Grüneisen parameter, GP. These two quantities, q and GP, are fundamental to the study of many basic phenomena in solids and to the prediction of a variety of physical properties like the equation of state.
8. A knowledge of lattice thermal expansion of a material is essential in investigations involving epitaxy and thin film growth and in thin film deposition in industry.

1.2. GRUNEISEN'S RELATION AND SECOND GRUNEISEN CONSTANT

Grüneisen (415) observed that for a large number of crystalline solids the coefficient of thermal expansion, α, should be proportional to the specific heat, C_v, over quite wide ranges of temperatures and even at low temperatures. This statement, known as the "*Grüneisen's rule*", can be expressed in the form

$$\frac{3\alpha}{\chi_T} = \gamma \frac{C_v}{V} \qquad (1.2.1.)$$

where χ_T is the isothermal compressibility of the solid, and γ is a dimensionless quantity, referred to as the *Grüneisen constant*. Grüneisen (415) from early expansion data gave values for the parameter, γ, generally in the vicinity of 2. γ was found to be independent of temperature.

The first-order volume derivative of γ is called the "*second Grüneisen constant*", q, to distinguish it from the normal Grüneisen parameter. It is expressed in the form

TABLE 1.1.

Crystal System	Axial relations	No. of constants	Thermal expansion tensor referred to axes in the conventional orientation
1. Triclinic	$a \neq b \neq c$ $\alpha \neq \beta \neq \gamma$	6	$\begin{bmatrix} \alpha_{11} & \alpha_{21} & \alpha_{31} \\ \alpha_{21} & \alpha_{22} & \alpha_{32} \\ \alpha_{31} & \alpha_{32} & \alpha_{33} \end{bmatrix}$
2. Monoclinic	$a \neq b \neq c$ $\alpha = \beta = 90^\circ$ $\gamma \neq 90^\circ$	4	$\begin{bmatrix} \alpha_{11} & 0 & \alpha_{31} \\ 0 & \alpha_{22} & 0 \\ \alpha_{31} & 0 & \alpha_{33} \end{bmatrix}$
3. Orthorhombic	$a \neq b \neq c$ $\alpha = \beta = \gamma = 90^\circ$	3	$\begin{bmatrix} \alpha_{11} = \alpha_1 & 0 & 0 \\ 0 & \alpha_{22} = \alpha_2 & 0 \\ 0 & 0 & \alpha_{33} = \alpha_3 \end{bmatrix}$
4. Tetragonal	$a = b \neq c$ $\alpha = \beta = \gamma = 90^\circ$	2	$\begin{bmatrix} \alpha_{11} = \alpha_1 & 0 & 0 \\ 0 & \alpha_{22} = \alpha_1 & 0 \\ 0 & 0 & \alpha_{33} = \alpha_3 \end{bmatrix}$
5a. Hexagonal (*Trigonal*)	$a = b = c$ $\alpha = \beta = \gamma \neq 90^\circ$, $< 120^\circ$		
5b. Hexagonal	$a = b \neq c$ $\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$		
6. Cubic and Isotropic	$a = b = c$ $\alpha = \beta = \gamma = 90^\circ$	1	$\begin{bmatrix} \alpha_{11} = \alpha & 0 & 0 \\ 0 & \alpha_{22} = \alpha & 0 \\ 0 & 0 & \alpha_{33} = \alpha \end{bmatrix}$

(Some authors distinguish, in different ways, an equivalence of the hexagonal system, calling it "*trigonal*" or "*rhombohedral*". M.J. Buerger points out in his book on "*Contemporary Crystallography*" that such practices lead to serious inconsistencies and should be avoided).

$$q = \left.\frac{\mathrm{d}\ln\gamma}{\mathrm{d}\ln V}\right)_{\mathrm{T}} \tag{1.2.2.}$$

1.3. THE NUMBER OF CONSTANTS IN VARIOUS CRYSTAL SYSTEMS

Thermal expansion coefficient, α, is a second-rank symmetric tensor relating temperature T (a scalar) and another second-rank tensor ε_{ik} (strain) by

$$[\varepsilon_{ik}] = [\alpha_{ik}]\cdot\mathrm{T} \tag{1.3.1}$$

where

$$[\alpha_{ik}] = \begin{bmatrix} \alpha_{11} & \alpha_{21} & \alpha_{31} \\ \alpha_{21} & \alpha_{22} & \alpha_{32} \\ \alpha_{31} & \alpha_{32} & \alpha_{33} \end{bmatrix} \tag{1.3.2.}$$

There are *six* crystal systems and the number of independent constants α_{ik} of the expansion coefficient depends on the system to which the crystal belongs. The maximum number of independent constants α_{ik} is six; but this number is reduced for crystals of higher symmetry. Wooster (1162) has deduced the number of constants for various crystal systems in his book on *Crystal Physics*. Accordingly, there are six constants for triclinic crystals, four for monoclinic, three for orthorhombic, two for tetragonal and hexagonal and one for cubic systems. The thermal deformation ellipsoid is a sphere in the cubic system and a spheroid of revolution in the tetragonal and hexagonal systems. In all crystals, except those belonging to the triclinic and monoclinic systems, the principal axes of the ellipsoid coincide with the principal crystallographic axes. In the triclinic and monoclinic crystals, the orientation of the ellipsoid with respect to the crystallographic axes is given by the additional number of constants. This orientation changes with temperature. The non-vanishing tensor components for the six crystal systems are given in Table 1.1.