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THERMAL EXPANSION OF PERICLASE AND OLIVINE,
AND THEIR ANHARMONIC PROPERTIES

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Thermal expansions of single-crystal periclase and olivine were measured

by a dilatometric method in a temperature range from room-leve1 to 1000℃.
The calculated thermal expansion coefficients of periclase and olivine are given in a range of temperature from -250 to 1500℃ based on the

Gruneisen's theory of thermal expansion. This theory involves several har-monic and anharmonic parameters. The parameters determined in this study are well related to acoustic wave velocities, pressure and temperature deri-vatives of bulk modulus, Gruneisen's parameter, which have been determined
by other means. It is shown that the accurate thermal expansion data pro-
vide a good estimation of elastic wave velocities and other physical constants,
which are important in the study of the equation of state of the deep interior
of the earth.

1. Introduction

Precise data of thermal expansion in the rock-forming minerals are of basic importance both in theoretical and experimental approaches to the clari-fication of the equation of state of the earth's interior.
Thermal expansion data are usually approximated by power series of temperature T. For example, KOZU et al. (1934) used the following equation for a linear thermal expansion Y(T),

Y(T)=a+bt+ctt2, (t=T-273.15) (1)
and SKINNER (1957),

Y(T)=a+bT=cTT2-d/T, (2)
where a, b, c, and d are constants and T in kelvin. However, these expres-sions of thermal expansion may not be appropriate to predict or to extrapolate the expansion at the temperatures out of the measured range.
The use of high-speed computers has made it easy to apply the Gruneisen's theory of thermal expansion to the analysis of the measured values (WACHTMANN et al., 1962). The merit of this approach is that the parameters obtained have physical meanings. The analysis enables us to have

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a basic understanding of harmonic and anharmonic properties of solids, and also to derive the other important physical constants relating to the equation of state.
In the present work, thermal expansions of single-crystal periclase and
olivine are measured on small pieces of specimen up to 1000℃ by means of

a high-sensitivity dilatometer. The analysis of the data of present and previ-ous works is made based on the theory, and the usefulness of this approach is discussed in connection with the physical constants of materials that are important in the study of the earth's mantle.

2. Theory and Calculation Procedure

GRUNEISEN (1926) derived the following theory of thermal expansion from the Mie-Gruneisen's equation of state,

PV+X(V)=γE, (3)

where P is pressure, X(V)=(dφ/dV)V, φ is a potential energy as a function
of volume only, γ is the Gruneisen's parameter regarded as constant, and E
is thermal energy of lattice vibration. At atmospheric pressures and above
temperatures higher than several tens of degrees kelvin, the first term of Eq.
(3) is very small compared with the right hand side and thus it is ignored in
this paper. The Taylor expansion of the second term with respect to volume
change Δ(=V-V0) is given by

(4)

where V0 is volume at 0 K. Irrespective of the functional form of potential
φ, we always have

(5)

where K0 is bulk modulus at 0 K. Combining Eqs. (3), (4), and (5), we obtain the representation of the volume expansion Y (T) as

(6)

where

(7)

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and

(8)

Q0 is also equal to the ratio of heat capacity to the thermal expansion coeffi-
cient at 0 K. It is emphasized that the results in Eqs. (6), (7), and (8) are
free from any assumption in the type of potentia1 φ. E is a function of tem-

perature and includes a characteristic temperature θ as a parameter. Thermal
expansion coefficient α0 is therefore derived as

(9)

This theory was applied to isotropic metals (GRUNEISEN, 1926) and also
to metals and simple compounds (KIRBY et al., 1972). The results show
better fit to experimental data than the use of Eq. (1) or (2). In the analysis
of thermal expansion data, Q0, k, and ƒÆ may be treated as adjustable con-
stants (HUME-ROTHERY, 1945).
WACHTMANN et al. (1962) modified Eq. (6) to anisotropic linear expansion
Yi (T) and obtained the relation

(10)

where ai is a parameter introduced to permit reference temperature being different from 0 K, and is defined by the ratio of a length of material along i-axis at reference temperature to that at 0 K. The quantities with suffix i are considered to depend on orientation i. Equation (10) is also used to ap-proximate volume expansion Y (T) and in this case, numerical factor 3 in denominator of right-hand side must be replaced by unity and "a" which appears in place of ai represents the volume ratio.

WACHTMANN et al. (1962) employed Nernst-Lindemann formula for E derived from a model with two phonon modes,

(11)

where p is the number of atoms in the molecular formula, and R is gas con-stant. One of the other expressions for E is given by Debye model of non-dispersive elastic solid with finite number of phonon modes,

(12)

where θ is the Debye temperature. After substituting either (11) or (12) into

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(10), we have an explicit expression of Yi (T) as a function of T. We can
obtain the parameter values of θi, Q0i, ki, and ai by fitting least-squares to
observed data.

In the present work, Eq. (12) is used instead of (11), since the use of (12)
for periclase and olivine gives better fittness than (11). Among various pa-
rameters, ki is sensitive to a selection of the energy function (11) or (12), and

yet the difference is about l percent.
Thermal expansion coefficient α0 of Eq. (9) or αr obtained by numerical
differentiation of Eq. (10) is transformed to an ordinary definition of α by

multiplying the factor 1/(1十Y(T)),

(13)

or

(14)

where Li is the length of material at T, and superscript 0 or r represents the
reference temperature of 0 or r K from which expansion is measured.

3. Experimental Procedure

3.1 Specimen

A periclase specimen (M-01) is a smoky synthetic piece of unknown
source and has low density (3.310g/cc) mostly due to considerable amount
of Ca content. Another periclase specimen (M-02) is a pure and transparent
one produced by W. & C. Spicer Co., and is reported to be free from infrared
absorption of iron (density=3.578g/cc).

The olivine single-crystal is taken out of a coarse grained lherzolite from
central Kenya in Africa. Forsterite component Fo (=Mg/(Mg+Fe+Mn))of

the crystal is 92.3 mol percent (SUWA et al., 1974) and density is 3.320g/cc
at 30℃.

Crystallographic orientation of the specimen is determined within an ac-
curacy of 1° by a Laue back-diffraction method and the sample is then cut
into a rectangular prism. The orientation of the two opposing surfaces of
the specimen are finished precisely parallel.

3.2 Apparatus

The apparatus used in this measurement is a high-temperature dilato-meter of type 8001H manufactured by Rigaku-Denki Co. The difference of elongations of a specimen and of a silica glass rod (reference) is detected by

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Fig. 1. Schematic illustration of the dilatometer.

a high-sensitivity differential transformer which is calibrated by a micrometer

screw. The mechanism of the apparatus is schematically shown in Fig. 1.

The differential elongation is recorded continuously on a strip chart

(width=250 mm) with a magnification of (1 or 2)×104 for a sample with
smaller length than 5mm length. The measurements are repeated several
times on the same specimen to confirm reproducibility.

Temperature is measured with a Pt-Pt/13% Rh thermocouple in contact
with the sample and recorded on the same chart mentioned above. The emf

of the thermocouple is calibrated by using the melting points of Pb (327.4℃)
and Ag (961.93℃). Errors in temperature readings were less than 2℃.

Olivine is measured in an inert gas environment in order to avoid the
oxidation of the specimen.

4. Experimental Results

4.1 Results of periclase-Check of the present method

To confirm the reliability of the present method, thermal expansion of

periclase were measured and compared with the data of other sources.

The values of thermal expansion of periclase specimens were read at the
20 or 50℃ interval and both corrections due to the blank test and the

expansion of the reference sample were made. The relative expansion data

referred to 30℃ are listed in Table 1. Applying Eq. (10) to the experimental

data of the linear expansion of the present and other sources, four parameters

θ, Q0, k, and a were determined by the least-square fitting and listed in
Table 2. Based upon the experimental formula for the thermal expansion

thus obtained, thermal expansion coefficients are obtained by numerical dif-

ferentiation. These values are shown together in Table 1.

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Table 1. The observed and calculated values of linear expansion and linear expan-sion coefficient of periclase.

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Table 2. Linear expansion parameters of periclase.

* Calculated from Reuss avg. of elastic constants given by SPETZLER (1970).

** Calculated from KT and density given by SPETZLER (1970) and γ (=1.54) given by
ANDERSON and ANDREATCH (1966).

+ Calculated from the pressure derivative of bulk modulus given by SPETZLER (1970).
++ Given by BARRON et al. (1959).

Fig. 2. Linear thermal expansion coefficient αγ vs. temperature for periclase. Calcu-

lated values of the present work are shown by smooth curves. Measuring methods
are shown by letters in parentheses, i: interferometer, x: X-ray powder method,
c: electric capacitance method, d: differential transformer.

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Table 3. The observed and calculated values of expansion and expansion coefficient
of olivine for each crystallographic direction and volume.

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The calculated values of thermal expansion coefficients are compared
with the results by different methods (AUSTIN, 1931; DURAND, 1936; SKINNER, 1957, GANESAN, 1962; WHITE and ANDERSON, 1966) in Fig. 2. Thick and thin lines in Fig. 2 are the fitted curves for present measurements. The extra-polated values are shown by broken lines. Both specimens give similar results and agree well with those of previous works. Especially, the results of the pure specimen (M-02) shows excellent agreement with those of the accurate interferometric method even in the extrapolated range of temperature. The data obtained by the X-ray method may not be accurate enough for com-parison.
This comparison in Fig. 2 shows that the present experimental technique
is reliable even for samples smaller than 10mm, and also that Eqs. (10) and
(12) are useful for analyzing the thermal expansion data.
4.2 Results of olivine

Olivine crystal has orthorhombic symmetry and has three independent

Fig. 3. Linear and volume thermal expansion coefficients αri vs temperature for
: numerical differentiation of ol ivine. Smooth curves: calculated values, symbols
the measured values.

Fig.3. Linear and volume thermal expansion coefficients αri vs temperature for
: numerical differentiation of
the measured values.

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Table 4. Expansion parameters of olivines.

* Calculated from elastic constants, density, and γ(=1.13) given by KUMAZAWA and
ANDERSON(1969). See text.

** Calculated from heat capacity data between 50 and 300 K, (KELLY, 1943).

values of thermal expansion corresponding to three directions perpendicular

to each other. The measured and calculated values of thermal expansion are

listed in Table 3. The thermal expansion coefficients directly calculated by

numerical differentiation of the measured expansion data are plotted in Fig. 3.

The smooth curves in the same figure are the calculated thermal expansion

coefficients αri obtained by the same procedure as that used for periclase.

Previously, thermal expansion of olivines has been reported by some

authors. KOZU et al. (1934) and SUWA (1964) measured it in large single-

crystals of chrysolite and fayalite by the dilatometric method. SKINNER (1962)

gave lattice parameters of synthetic forsterite measured at high temperature
by the X-ray powder method. All these data on thermal expansion of olivines

are analyzed and the parameters thus determined are listed in Table 4 for

comparison. The result of the present measurement gives the smallest standard

deviation for each direction among all the data published up-to-date. Further,

it gives the appropriate values for each parameter as discussed in next section.

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5. Discussion

5.1 Comparison of the parameters with those from other sources

Debye temperature in Eq. (12) is defined by maximum frequency νmax of

phonon modes in the lattice and represented by acoustic wave velocities,

(15)

where h and kB are Plank and Boltzmann constants, respectively. N is

Avogadro number, M is molecular weight, ρ is density, and VP and VS are

longitudinal and transverse wave velocities, respectively. When we employed

the reported values of VP=8.36 and VS=4.84km/s (KUMAZAWA and

ANDERSON, 1969) for the acoustic wave velocities, the calculated value of θ

was 732K. On the other hand, the Debye temperature calculated from heat

capacity data between 50 and 300K (KELLY, 1943) for synthetic forsterite

was 780K. These values are in good agreement with 705±37K of the

present result for volume expansion. Debye temperatures from the other
thermal expansion data are too large compared with those expected from the

acoustic and calorimetric data.

The maximum frequency of phonon having a wave vector parallel to each
crystallographic orientation might be represented in the same way as Eq. (15).

The orientation dependency of θ is calculated from acoustic data of olivine,

and is compared with those obtained from the thermal expansion data in Table

5. For olivine, it is expected that Debye temperatures determined by expan-
sion data of different orientations should not be very diverse. In Table 4,

Table 5. Comparisons of anisotropic properties from present thermal expansion data with those from elastic constants* for olivine.

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Debye temperatures for different orientations of forsterite, chrysolite, and

fayalite all in olivine group are extremely scattered except those of the present

peridot specimen. The source of this difference is attributed probably to the
accuracy of tha original data.

Q0 is defined in Eq. (7). Among the three quantities appearing in the
right-hand side of (7), the value of γ at 0 K is the most difficult to estimate

accurately. However, all of them do not change appreciably with temperature,

and the values of olivine under ambient conditions (V=43.95cc/mol, KT=

1.262 Mbar, γ=1.13, KUMAZAWA and ANDERSON, 1969) are used to evaluate

Q0. The result is Q0=4.91(×106J/mol), which is in excellent agreement with
the present value of 5.15±0.08.

Equation (7) is simply extended to orientation-dependent quantities as

(7')

where βi and γi are linear compressibility and Gruneisen's parameter in ori-

entation i, respectively. Assuming that γi does not depend on orientation and

replacing γi with γ (=1.13), we may calculate the linear compressibilities of

olivine. Despite of a crude generalization of (7'), their considerable agree-

ments with acoustic compressibilities are observed in Table 5.

In Eq. (8), the pressure derivative of the isothermal bulk modulus ∂KT/∂P
is connected with k at 0K. Therefore, the value of k is independently evalu-

ated from ∂KT/∂P of the other sources. The ∂KT/∂P of olivine at room tem-

perature is reported as 5.1 (KUMAZAWA and ANDERSON, 1969) and thus k=
2.05. The present value of k=2.67±0.24 is regarded as close to expected

value of 2.05, when we consider the inadequacy of determining k from the

therrnal expansion data in a limited temperature range. For an accurate

determination of k from thermal expansion data, it is necessary to measure

it in a wider range of temperature higher than the Debye temperature since

the value of ∂Y(T)/∂k rapidly increases with temperature and has sufficiently
large magnitude above the Debye temperature.

The other interpretation on the difference in k values between different
sources is that ∂KT/∂P in Eq. (8) should have been evaluated at 0K. The

value of (∂KT/∂P)T=0K is expected to be higher than that at room temperature,

since it increases with decrease of temperature in the case of periclase

(ANDERSON and ANDREATCH, 1966; SPETZLER, 1970).
The ∂KT/∂P of inorganic solid materials usually exceeds 3, and thus k

should be larger than unity. The values of k in chrysolite and fayalite are

determined to be less than unity (Table 4) and so the original data might

include some ambiguity especially at higher temperature.

Equation (8) is represented by linear quantities as

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(16)

for isotropic materials, where βi is a linear compressibility. In analogy of

Eq. (16), the pressure derivatives of linear compressibilities are calculated by

(17)

and compared with those obtained from the acoustic data in Table 5. The

correlation is faily good, whereas (2kc+1) looks somewhat small.
As discussed in above, a number of physical constants derived from the

thermal expansion data are quite well correlated with those calculated from

calorimetric and acoustic data even for the anisotropic properties. Such re-

lationship has never been recognized significantly before.

Similar comparisons of θ, Q0, and k of periclase specimens are made in

Table 2. The result is excellent in the case of pure specimen (M-02) except

for a difference of 200 K in θ.

The comparisons of θ, Q0, and k of thermal expansion with those calcu-

lated from elastic and calorimetric data on both olivine and periclase stated

above suggest that the present thermal expansion data and the present method

of analysis are valid. lt seems likely that the accurate determination of ther-

mal expansion of materials and appropriate way of analyzing them are quite

useful for clarifyin the harmonic and anharmonic properties of solids.

5.2 Application

In order to clarify the constitution of the earth mantle, it is essential to

know several physical constants such as acoustic wave velocities, their tem-

perature and pressure derivatives, etc. for the materials that are inferred to
be present in the earth's interior. However, sufficient amounts of the materials

are not always accesible to enable us to measure the physical properties.

When we know the density and mean atomic weight of such materials, we

may estimate the bulk modulus with considerable reliability by using Birch's

systematics or its modification (SHANKLAND and CHUNG, 1974). However,

such properties as rigidity, Gruneisen's parameter, pressure and temperature

variation of the elastic constants are neither measured on the materials that

are available only in a limited volume, nor estimated with sufificient reliability

based on any established systeanatics in these quantities.

One of approaches in resolving this difficult situation is proposed in this

paper; that is, the precise measurement of thermal expansion by X-ray dif-
fraction method and the analysis of the data based on an appropriate theory,

Supposing that we know only the znean atomic weight, bulk modulus,

density and thermal expansion data (θ, Q0, and k) for olivine, we try to deter-

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mine the other physical constants from these data. We can predict rigidity

(and thus shear wave velocity) from Debye temperature by a method presented by ANDERSON (1965). The result is 0.725 Mbar (VS=4.64km/s) which is very close to 0.7752 Mbar (4.839km/s) determined experimentally (KUMAZAWA and ANDERSON, 1969). The value of r is calculated as 1.07 from Q0, KT and V. The pressure derivative 6.34 of bulk modulus calculated from k is a little larger than that measured, but is not such a bad estimation. The Gruneisen-Anderson's parameters;

are also calculated as

Both δs and δT are in good agreement with 4.93 and 6.68, respectively, which
are determined experimentally from temperature derivatives of bulk modulus

(KUMAZAMA and ANDERSON, 1969). Then the temperature derivatives of bulk
modulus are very precisely predicted (e.g., ∂KS/∂T=-1.76(×10-4 Mbar/deg.)
in the present prediction; -1.55 and -1.78 determined by KUMAZAWA and
ANDERSON (1969), and GRAHAM and BARSCH (1969), respectively at room
temperature).

Stishovite may be one of the most important materials in the earth's
mantle. Hence we try to apply the same procedure to the thermal expansion
data of stishovite measured by the X-ray method (ITO et al., 1974). Debye
temperature and Q0 are found to be 1025K and 2.93 (×106J/mol), respec-
tively, which may be well compared with 920K and 3.20 calculated from
the acoustic wave velocities by MIZUTANI et al. (1972). γ is also estimated
by using Eq. (7) and is 1.67. This is comparable with 1.52 of thermal
Gruneisen's parameter (ITO et al., 1974). However, the negative values of k
are derived both for volume and for respective crystallographic orientations.
This difficulty certainly stems from the large scattering of the experimental
data and also from the narrow temperature range of measurement. More
accurate data in wider temperature range are necessary to be able to derive
useful information from the thermal expansion data.

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