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Thermal Expansion of Rutile from 100 to 700 °K*

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The thermal expansion of a single crystal of rutile (TiO_2) was determined in directions parallel to its crystallographic axes. A unique macroscopic technique was used wherein a cube-shaped specimen was cut from the anisotropic crystal, each of its six faces polished flat and nearly parallel to the face opposite it, and the expansion measured along each of its three body axes with an Abbe-Pulfrich interferometer. The relationship between the expansion along the body axes of the specimen and that in the crystallographic directions was determined from a Laue x-ray pattern. The unusual behavior of the thermal expansion that was observed can be explained by assuming an acoustical and optical contribution where the corresponding Grüneisen constants are 2.80 and 0.75 respectively.

Key Words: Anisotropic crystal, Grüneisen's constant, interferometer, rutile, thermal expansion.

1. Introduction

Thermal expansion is the dimensional change of a body which occurs with change in temperature. Grüneisen [1][1] has shown that the thermal expansion of a Debye solid should be approximately proportional to the internal energy. It has been found experimentally [2, 3, 4] that Grüneisen's relation is generally true for those elements that crystallize in face-centered-cubic, body-centered-cubic, close-packed-hexagonal, and tetragonal structures.

At present, interest [5] is being shown in solids which deviate from Grüneisen's relation. These solids include those that crystallize in a diamond-cubic structure (Ge, Si, diamond, InSb, etc.) and some glasses (vitreous silica, borosilicate, etc.). Theories have been proposed to explain the unusual behavior of these materials. Diamond-structure solids for instance are said to have a low-lying transverse acoustic mode which at low temperatures is predominant in absorbing energy. Glasses that have negative expansivity are said to have a low-lying transverse optical mode which also absorbs energy at low temperatures. The large effect of the transverse modes in all of these materials is due to open structures which result in large values of the shear elastic compliances associated with the modes [6].

The analysis of recent measurements of thermal expansion of rutile (TiO_2) with an x-ray technique [7] and a dilatometric technique [8] has indicated that the expansion of this material also deviates from the simple Grüneisen relation. This deviation is opposite to that of the above mentioned materials in that the expansivity at low temperatures seems larger than expected. Because these measurements were not of high precision, a precise determination of length, of the order of one part per million, was desired. This paper describes a unique set of thermal expansion measurements on a single crystal of rutile from 100 to 700 °K to obtain the desired precision.

2. Apparatus

X-ray techniques are often the preferred way, and for certain crystals (triclinic and monoclinic) perhaps the only way, to measure the thermal expansion of an anisotropic crystal. The difficulty of obtaining accurate measurements of lattice spacings versus temperature [9], however, occasionally makes the use of macroscopic techniques preferable. Determinations of anisotropic expansion with macroscopic techniques [10, 11] have almost always been made on two or more single crystals of the material having different orientations between the specimen axis and the crystallographic axis. In the case of materials like rutile, which are grown at high temperatures, differences in residual strain and lattice defects may occur between specimens grown in different crystalline directions. To eliminate some errors that might be caused by such differences, an Abbe-Pulfrich interferometer [12] was used to measure the thermal expansion along three nearly orthogonal directions of a single-crystal specimen of rutile. The only known use of this technique was by Benoit [13] in 1888 on a cube-shaped specimen of crystal quartz used in his determination of the density of water.

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*This paper is based in part on a thesis submitted to the Department of Physics and Astronomy of the University of Maryland in partial fulfillment of the requirements for an M.S. degree, 1964.

[1] Figures in brackets indicate the literature references at the end of this paper.

The assembled interferometer and its individual parts are shown in figure 1. Three ruby spheres, each resting on a small flat area polished on one side, are placed on an optical flat. The cube-shaped specimen, about 12 mm on a side, rests on the three ruby spheres. An etalon made from recrystallized W–1 tool steel supports the top flat. The dimensions of the ruby spheres (about 3 mm) are adjusted so that Fizeau fringes, fringes of equal thickness, can be obtained between optical flats when separated by them. The dimensions of the steel etalon (about 16 mm) are adjusted in the same way. Parallelism between opposing faces of the rutile specimen is such that Fizeau fringes are also obtained in the completely assembled interferometer between the specimen's upper face and the top flat.

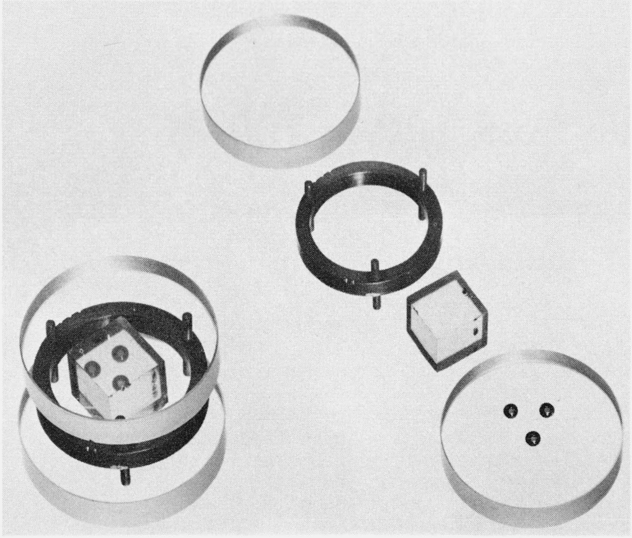

FIGURE 1. *Assembled interferometer and the individual parts.*

The fringes were observed with a Pulfrich viewer and their displacement from a reference point engraved on the lower surface of the top flat was measured with a filar-micrometer eyepiece. The filtered green line of a natural mercury discharge lamp was used for illumination.

Temperatures below 300 °K were measured with a copper-constantan thermocouple while higher temperatures were measured with a chromel-alumel thermocouple. A potentiometer was used to measure the emf of the thermocouples to 1 μV. The thermocouples had been calibrated by the Temperature Physics Section of the National Bureau of Standards. The cryostat and furnace used are shown in figures 2 and 3.

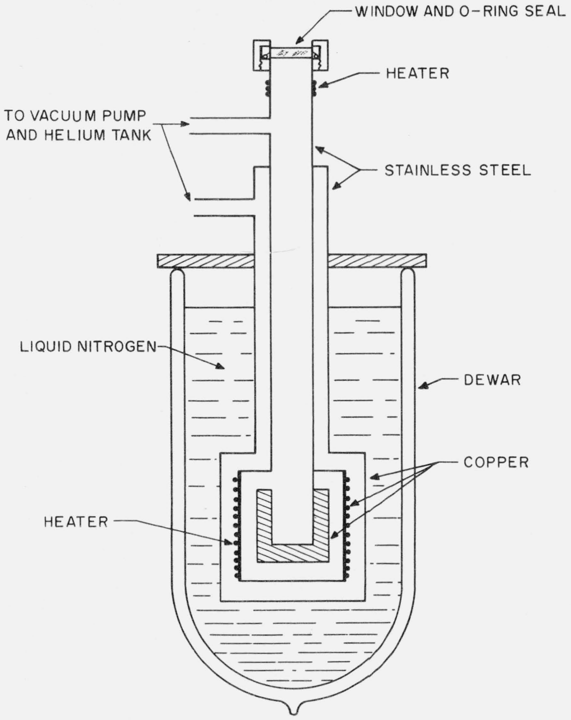

FIGURE 2. *Schematic drawing of the cryostat.*

The heavy copper block in which the interferometer is placed is suspended by three thin strips of stainless steel, only one of which is shown.

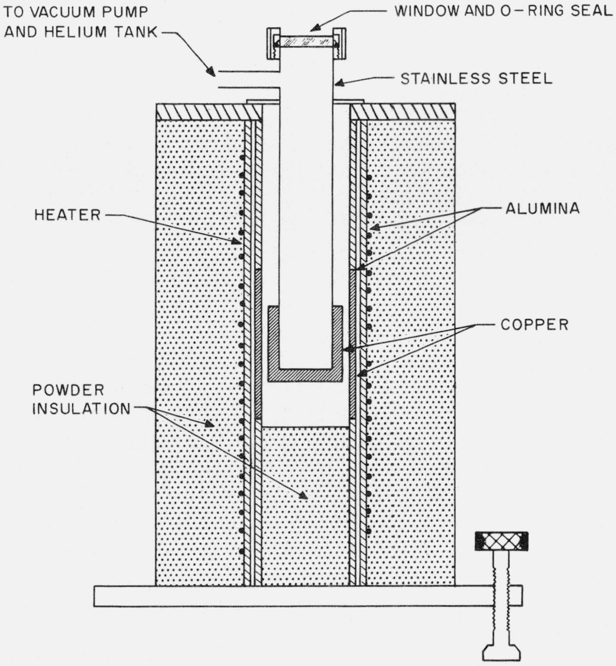

FIGURE 3. *Schematic drawing of the furnace.*

3. Specimen

The rutile crystal, obtained from the National Lead Company, was grown by the Verneuil flame fusion technique and may contain as much as 0.1 percent of impurities. The color of the crystal is faintly yellowish which indicates that it is nearly stoichiometric. The specimen was cut from the boule with a diamond saw and the opposite faces were made nearly parallel by precision grinding. The six faces were then carefully lapped to optical flatness. When interference was observed between opposite faces of the specimen the fringes were distorted by local variations in the index of refraction. The ordinary and extraordinary rays, however, could be clearly extinguished with a polaroid filter and a grid pattern was not visibly distorted when viewed through the specimen. The density of the specimen was determined by a direct measurement of its mass and dimensions and was found to be 4.24 g/cm^3.

The body axes normal to the faces of the specimen are nearly orthogonal to one another. The angles between them as determined with an autocollimator are $\phi_{XY}=89°51'$, $\phi_{YZ}=89°30'$, and $\phi_{ZX}=90°2'$. A back-reflection Laue x-ray pattern was used to determine the inclination, ω, of the body axes from the crystallographic c direction. Values of ω are given in table 1.

TABLE 1. *Angle of inclination between the crystallographic c direction of the rutile specimen and each of its body axes*

Body axis	ω
X	17.2°
Y	72.9°
Z	86.9°

4. Experimental Procedure

Measurements of temperature and of fringe positions were made at intervals of about 50 °K only when the system was at constant temperature as indicated by the fringes remaining stationary for at least 15 min. The expansion observed in the complete interferometer is the difference between the expansion of the steel etalon and the sum of the expansions of the ruby spheres and the specimen. Since fringes could be obtained between the optical flats when separated by either the ruby spheres or the steel etalon the values for their expansion were determined in separate tests with the same equipment.

The expansion is measured by determining the number of fringes, N, passing the reference point.

$$\Delta L=\frac{N\lambda_r}{2}+A_c$$

where $\lambda_r=0.54623$ micrometer is the wavelength of the green line of mercury in vacuum. The apparent expansion, A_c, caused by the change in the index of refraction of the gas when subjected to a temperature change may be estimated from the following equation based on the ideal gas laws [14].

$$A_c=\frac{(n_0-1)288LP(T_2-T_1)}{760T_1T_2}$$

where n_0 is the index of the gas at standard conditions, L is the separation of the optical flats, P is the pressure (torr), and T_1 and T_2 are the initial and final temperatures (degrees Kelvin). This apparent expansion may be made small by operating at a low pressure. Since the index, n_0, of helium is 1.000036, the value of A_c will be negligible for the measurements presented here when the pressure is less than 5 torr. All of the measurements of expansion were made in a helium atmosphere at a pressure of about 2 torr which is sufficient to support good heat transfer.

While heating between observation temperatures the number of fringes that passed the reference point was carefully observed. The length at each temperature was measured with a precision of ±0.03 of a fringe (±0.008 micrometers). Each run was repeated until the measurements of length at each temperature did not differ by more than 1/10 of a fringe. A smoothed curve of the expansion for each direction in the specimen, for the ruby spheres, and for the steel etalon was obtained by a procedure such that there was overall agreement with the observed data as well as agreement between coefficients taken from it at 50 degree intervals and the coefficients calculated from the observed data.

5. Experimental Results

Smoothed curves representing the expansion of the ruby spheres, the steel etalon, and the specimen are shown in figure 4. No attempt was made to determine

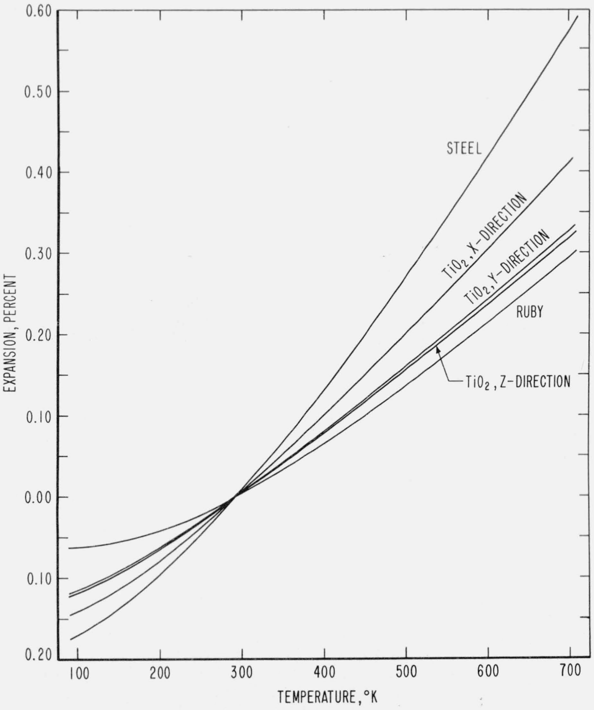

FIGURE 4. *Linear thermal expansion of the cube-shaped rutile specimen in the direction of its body axes* X, Y, *and* Z, *of the W–1 tool-steel etalon, and of the ruby spheres.*

the crystallographic orientation of the ruby spheres but their average expansion as determined is in excellent agreement with the results of Wachtman et al. [10] on the expansion of polycrystalline aluminum oxide. Values obtained for the thermal expansion of the W–1 tool steel, given in table 2, are in good agreement with results obtained on other medium-carbon steels [15].

TABLE 2. *Thermal expansion of recrystallized W–1 tool steel*

Temperature	Linear thermal expansion
°K	*Percent*
100	−0.1703
150	−.1386
200	−.0958
250	−.0465
293	.0000
300	.0079
350	.0670
400	.1303
450	.1976
500	.2683
550	.3420
600	.4182
650	.4965
700	.5767

It can be shown for rutile, which has a tetragonal crystal structure (P4/mnm), that only two coefficients are needed, α_a and α_c, to represent the expansion of the crystal. Volume expansivity is given by

$$\beta = 2\alpha_a + \alpha_c$$

while expansivity in a direction inclined at an angle ω from the c axis is given [16] by

$$\alpha_\omega = \alpha_a + (\alpha_c - \alpha_a) \cos^2 \omega.$$

The linear expansion is given by

$$\left(\frac{\Delta L}{L}\right)_\omega = \left(\frac{\Delta L}{L}\right)_a + \left[\left(\frac{\Delta L}{L}\right)_c - \left(\frac{\Delta L}{L}\right)_a\right] \cos^2 \omega. \quad (1)$$

Values of $\left(\frac{\Delta L}{L}\right)_a$ and $\left(\frac{\Delta L}{L}\right)_c$ were obtained by fitting equation (1) to the smoothed values of $\left(\frac{\Delta L}{L}\right)_X$, $\left(\frac{\Delta L}{L}\right)_Y$, $\left(\frac{\Delta L}{L}\right)_Z$, and the corresponding values of ω by the method of least squares. These values are given in table 3.

The results of this investigation are in good agreement with results of other investigators [7, 8, 17, 18, 19] as indicated in figure 5 where values of the expansivities α_a and α_c are plotted against temperature.

TABLE 3. *Thermal expansion of rutile* (TiO_2)

Temperature	Body axis			Crystallographic direction		Volume
	X	*Y*	*Z*	*c*	*a*	
°K	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*
100	−0.1414	−0.1184	−0.1157	−0.1439	−0.1158	−0.3751
150	−.1140	−.0941	−.0921	−.1161	−.0920	−.2999
200	−.0782	−.0642	−.0625	−.0797	−.0626	−.2049
250	−.0375	−.0307	−.0299	−.0383	−.0299	−.0981
293	.0000	.0000	.0000	.0000	.0000	.0000
300	.0063	.0051	.0050	.0064	.0050	.0164
350	.0526	.0428	.0416	.0537	.0417	.1372
400	.1007	.0817	.0793	.1029	.0795	.2621
450	.1503	.1212	.1177	.1535	.1179	.3899
500	.2010	.1611	.1567	.2052	.1568	.5197
550	.2526	.2019	.1966	.2579	.1966	.6524
600	.3049	.2436	.2373	.3114	.2372	.7878
650	.3576	.2861	.2785	.3653	.2785	.9251
700	.4106	.3290	.3201	.4193	.3202	1.0635

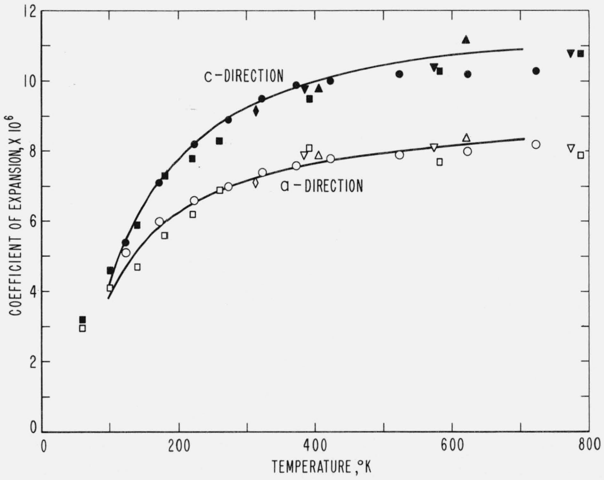

FIGURE 5. *Expansivity of rutile in the crystallographic directions.*

The results of this investigation, as represented by the curves, are compared with the results obtained by Mauer and Bolz □, Kirby ○, Grain and Campbell △, Merz ▽, and Fizeau ◊.

6. Discussion

The usual expression for Grüneisen's parameter is

$$\gamma(T) = \frac{\beta V}{C_p \kappa_s}$$

where β is the coefficient of volume thermal expansion, V is the molar volume, C_p is the molar heat capacity at constant pressure, and κ_s is the adiabatic compressibility. The value of $\gamma(T)$ for well-behaved materials increases slightly from low to high temperatures such that $\gamma(\infty) - \gamma(0) \leq 0.3$ [20]. The unusual behavior of rutile is indicated in figure 6 where the experimentally determined value of $\gamma(T)$ decreases from 2.6 at 100 °K to a high-temperature value of 1.47. Values of $\gamma(T)$ plotted in this figure are listed in table 4. The molar volume at room temperature was calculated from unit cell parameters as determined by Baur [21], the molar heat capacity was calculated by averaging the data of Shomate [22], McDonald and Seltz [23], and Naylor [24], and the compressibility was calculated from the measurements of Chung [25].

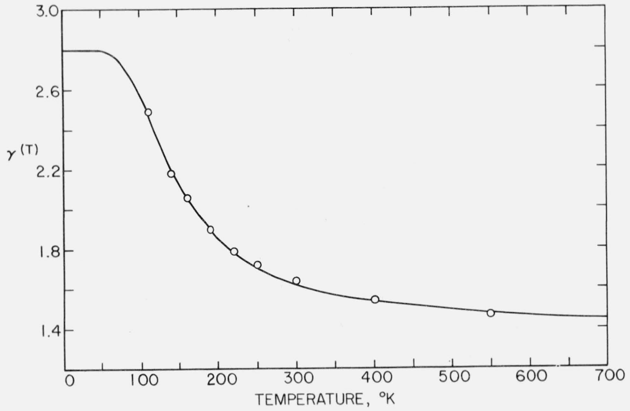

FIGURE 6. *Grüneisen parameter for rutile.*

TABLE 4. *Grüneisen parameter and values for expansivity, volume, heat capacity, and compressibility*

Temperature (T)	Coefficients of linear thermal expansion (α_a)	(α_c)	Coefficient of volume thermal expansion (β)	Molar volume (V)	Molar heat capacity (1 cal = 4.1840J) (C_p)	Adiabatic compressibility (κ_s)	Grüneisen parameter (γ)
°K	10^{-6}/°K	10^{-6}/°K	10^{-6}/°K	cm³/mol	cal/mol °K	10^{-13} cm²/dyn	
110	4.30	4.89	13.49	18.74	5.10	4.750	2.49
140	5.07	6.04	16.18	18.75	7.00	4.753	2.18
160	5.51	6.66	17.68	18.76	8.09	4.756	2.06
190	6.02	7.43	19.47	18.77	9.64	4.761	1.90
220	6.43	8.04	20.90	18.78	10.97	4.768	1.79
250	6.76	8.55	22.07	18.79	12.10	4.776	1.72
300	7.18	9.21	23.57	18.81	13.51	4.795	1.64
400	7.67	10.00	25.34	18.86	15.29	4.851	1.54
550	8.11	10.56	26.78	18.93	16.56	4.961	1.47

Grüneisen's relation can be expressed as

$$\beta = \frac{\gamma C_v \kappa_T}{V} = \kappa_T \left(\frac{\partial S}{\partial V}\right)_T$$

where C_v is the molar heat capacity at constant volume, κ_T is the isothermal compressibility, and S is the entropy. Since entropy is an additive function of state Grüneisen's relation can be interpreted as a sum

$$\beta = \frac{\kappa_T}{V} \sum_i \gamma_i C_i. \tag{2}$$

This approach has been successfully used to determine the contributions to thermal expansion from conduction electrons [26] and magnetic spin interactions [27] as well as from the lattice. In order to make sense out of the expansion data for rutile it is suggested that for polyatomic crystals eq (2) can also be used to determine the contributions to thermal expansion from the acoustical and optical modes of lattice vibrations.

Since the heat capacity of rutile can be represented to within a few percent from 50 to 600 °K by the combination of a Debye and a single Einstein expression it was hoped that by analogy only two terms for the expansion would be sufficient,

$$\beta = \frac{\kappa_T}{V} (\gamma_{\text{aco}} C_{\text{aco}} + \gamma_{\text{opt}} C_{\text{opt}}), \tag{3}$$

instead of three that might be expected (one acoustical and two optical). The validity of eq (3) for rutile has been tested graphically by plotting $(\beta V / C_{\text{aco}} \kappa_T)$ against $(C_{\text{opt}}/C_{\text{aco}})$, see figure 7. It can be seen that a straight line fits the data as hoped. The intercept of the line with the vertical axis at $C_{\text{opt}}/C_{\text{aco}} = 0$ gives a value of 2.80 for γ_{aco} while the slope of the line gives a value of 0.75 for γ_{opt}.

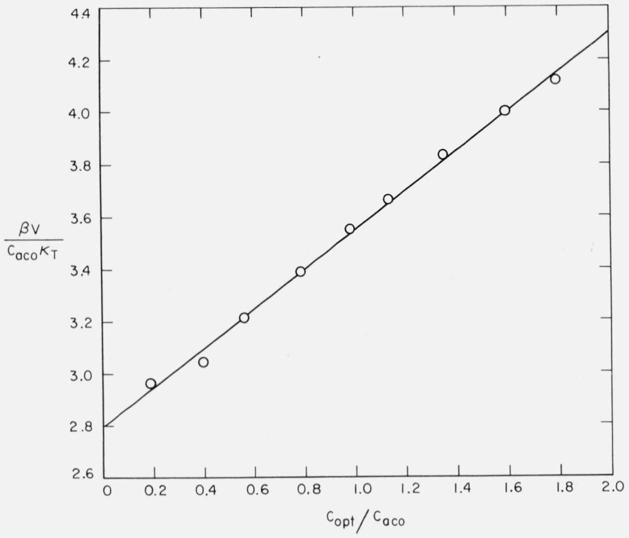

FIGURE 7. *Confirmation that the contributions of the acoustical and optical modes of lattice vibrations to the thermal expansion of rutile can be separated.*

Values for C_{opt} were calculated from the Einstein expression for heat capacity, $C_{\text{opt}} = 2C\left(\frac{\theta_E}{T}\right)$, using 706 °K as the characteristic temperature. This value for θ_E agrees very closely with the infrared resonance frequency at the absorption maximum [28]. Values for C_{aco} were calculated by taking the difference between observed values of C_v and calculated values of C_{opt}.

The temperature variation of $\gamma(T)$ can be calculated from

$$\gamma(T) = \frac{\gamma_{\text{aco}} C_{\text{aco}} + \gamma_{\text{opt}} C_{\text{opt}}}{C_v}$$

and is represented by the solid line in figure 6. At temperatures below 60 °K, $\frac{\theta_E}{T} \sim 12$, the values of C_{opt} are very small and in the limit as $T \rightarrow 0$ °K,

$C_{opt}/C_{aco}=0$, it can be seen that $\gamma(0) \sim \gamma_{aco}=2.80$. At high temperatures $C_{aco}\rightarrow 1/3C_v$ and $C_{opt}\rightarrow 2/3C_v$ and in the limit as $T\rightarrow\infty$, $C_{opt}/C_{aco}=2$, it can be seen $\gamma(\infty)=1/3(\gamma_{aco}+2\gamma_{opt})=1.43$.

The plots of $\frac{3\alpha_c V}{C_{aco}\kappa_T}$ and $\frac{3\alpha_a V}{C_{aco}\kappa_T}$ versus C_{opt}/C_{aco} can also be represented by straight lines with the resulting values at 1.06 and 0.60 for γ_{opt} and 3.04 and 2.68 for γ_{aco} respectively. These results indicate that the value of α_c will always be larger than the corresponding value of α_a.

Using the definition of expansivity as the temperature derivative of the elastic strain tensor at constant stress it can be shown [29] that the principal γ-values for a tetragonal crystal are represented by

$$\gamma_1=\frac{V}{C_p}[(c_{11}+c_{12})\alpha_a+c_{13}\alpha_c]$$

$$\gamma_3=\frac{V}{C_p}(2c_{13}\alpha_a+c_{33}\alpha_c).$$

Since the values of the elastic constants are only known at room temperature [30] the temperature dependence of γ_1 and γ_3 can not be evaluated. Their values at 300 °K, however, are 1.5 and 2.1 respectively.

According to Barron and Leadbetter [31] the volume dependence of certain properties of a crystal, for instance the characteristic temperature for the entropy,

$$\frac{\theta^s(V_0)}{\theta^s(V)}\sim\left(\frac{V}{V_0}\right)^{\gamma_n}\text{where } n=0,$$

and the characteristic temperature for the Debye-Waller factor for x rays,

$$\frac{\theta^M(V_0)}{\theta^M(V)}\sim\left(\frac{V}{V_0}\right)^{\gamma_n}\text{where } n=-2,$$

depend in a direct manner on individual moments of the frequency distribution, $\overline{\nu^n}$. The dimensionless parameters, γ_n, are defined as

$$\gamma_n=-\frac{1}{n}\frac{d\ln\overline{\nu^n}}{d\ln V}.$$

It can be shown that $\gamma_{-3}=\gamma(0)=2.80$ and $\gamma_0=\gamma(\infty)=1.43$, the low and high temperature limiting values of the Grüneisen parameter. At intermediate temperatures

$$\gamma_n=\int_0^\infty\gamma(T)C_vT^{n-1}dT\Big/\int_0^\infty C_vT^{n-1}dT$$

where $-3<n<0$. Using Simpson's rule to evaluate these integrals it was found that γ_{-2} and γ_{-1} are equal to 2.58 and 2.07 respectively.

7. Conclusions

The thermal expansion of an anisotropic crystal, rutile, has been determined from 100 to 700 °K with a unique macroscopic technique. These measurements of expansion (length) are estimated to be accurate to within 4 ppm.

In analyzing these measurements it has been shown that the expansion of rutile is the result of contributions from the acoustical and optical modes of lattice vibrations. Acoustical vibrations seem to be about twice as effective as optical vibrations in causing the volume expansion of the crystal while the optical vibrations are slightly more effective in the direction parallel with the *c* axis than in a perpendicular direction.

There is reason to assume that the thermal expansion of polyatomic crystals in general will to some degree be dependent upon optical modes of vibration as well as upon acoustical modes [32].

The author is indebted to J. B. Wachtman, Jr., for supplying the rutile crystal and information on its crystallographic orientation and to D. H. Chung for allowing the use of his unpublished elasticity data without which the analysis could not have been made. The author is also grateful to T. A. Hahn for interesting and helpful discussions about this work and to J. W. McDermott for the difficult job of preparing the specimen.

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