

THE CONSTANTS OF ALPHA QUARTZ (1992 Update)

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SUMMARY

Anyone performing calculations on quartz crystal devices requires numerical values for the physical constants used in his equations. However, as with any physical constant, there is no absolute value which may be assigned to a constant of quartz—only a "best" value based upon numerous observations performed under controlled laboratory conditions on a variety of documented samples.

With time, and much effort, the quartz engineer accumulates his own list of "best" values for the frequently used constants of quartz. Still, when a new calculation involves an obscure constant, a literature search is required to find that obscure value.

Such a literature search has been conducted, and a list of "good" constants for alpha quartz is presented.

NOMENCLATURE

The word "quartz" as used herein means electronic grade crystalline SiO_2 at temperatures below 573°C , either natural or man-made (cultured).

Historically, the term rock crystal, low-quartz, alpha quartz, or crystalline quartz has been used for "quartz".

Modern usage in certain industries uses the term "quartz" to refer to fused quartz—quartz which has been heated to above its melting point (1710°C). Fused quartz is non-piezoelectric and non-crystalline; hence, of no usefulness to the quartz engineer. Sosman [1], p. 43, says: "The use of the single word "quartz" to refer to vitreous silica can not be too strongly condemned. It has arisen through carelessness or ignorance and is already [1927!] causing troublesome confusion." Sosman suggests the use of "quartz-glass" or "fused quartz" for this material.

Some quartz engineers refer to cultured (man-made) quartz as "synthetic" quartz. Synthetic gives the connotation of "not real", so is to be avoided in this context, since cultured quartz is "real" quartz.

HISTORY

Ever since man first held a piece of quartz in his hand, he has been aware of one of quartz' physical constants—its density. Since then, most physical constants of quartz have been studied and measured. There are thousands of references in the literature on the subject. Many of the measurements are of little value today since details of the experiments were often neglected—i.e., temperature, source of the quartz, measurement standards, etc.

Quartz obtained from most locations is not useful for electronic applications, due to excessive twinning, inclusions, and fracturing. Through World War II, all quartz used was natural quartz, mostly from Brazil. Since then, the art of culturing quartz has evolved to where today cultured quartz is used almost exclusively for electronic applications.

The constants presented here may be applied to only the finest grades of cultured quartz—those that most nearly imitate natural quartz. Devices fabricated from lower quality cultured quartz have physical constants enough different from natural quartz to produce sizeable errors when compared to otherwise identical natural quartz devices.

ACTUAL DEVICES

Due to the assumptions used in any theory, and also due to the probability that the calculated device has a different geometry (diameter, contour, electrode size) than the units measured to produce a given physical constant, and due to manufacturing tolerances (especially angular orientation) it is usually impossible to theoretically predict quartz device behavior to better than an equivalent angular orientation of about $\pm 1/2^\circ$ for double-rotated cuts.

Some researchers have used microwave measurement techniques to determine the elastic stiffnesses, and their temperature coefficients, of bulk quartz—often 1 inch cubes of carefully oriented quartz

samples. Other researchers have called for more precise measurements, over extended temperature ranges, to be performed. (See, for example, [20].) But such a set of constants cannot predict the behavior of real-world resonators to an accuracy of better than approximately 30 arc minutes!

To better refine a theory, it is necessary (and it will always be necessary) to make a matrix of actual, real-world devices—all of the same physical design, except for a well controlled slight variation in orientation.

For example, EerNisse[2] in 1975 predicted the SC-cut to occur at $\phi=22^{\circ}30'$. Kusters and Leach [3] experimentally showed that for their crystal design, $\phi=21^{\circ}56'$, a variation of $34'$. Kusters and Leach determined ϕ by a carefully controlled experiment involving a matrix of orientations about EerNisse's predicted angle, careful measurements, and computer reduction of the data to define the orientation for the zero thermal transient effect (assuming that the in-plane stress of EerNisse is the same mechanism measured by Kusters and Leach in their thermal transient tests).

Similarly, Adams et al.[4] determined the temperature coefficients of the elastic stiffnesses of quartz, using a matrix of precisely oriented, identically prepared resonators, as opposed to Bechmann's et al.[5] determination of the same coefficients using a varied assortment of crystal designs of moderate orientational precision. And yet, neither set of constants can predict the temperature behavior of the SC-cut, as actually manufactured, to better than an equivalent angular orientation of $1/2^{\circ}$; but both can be used to predict the existence of, and the shape of, the temperature curve for the SC-cut, and do so accurately enough to allow the experimental cuts to be selected with enough precision to "close the loop" with only one or two iterations of the actual devices! What more could one ask?

Similar experimental tests will always be required to ultimately define a desired quartz device orientation. (Unless the theory can be expanded to include the now unsolvable effects of the boundary conditions: finite diameter, contoured surfaces, film stress, mounting stress, etc.)

THE CONSTANTS

In 1927, Sosman[1] published 800 pages devoted to the physical properties of silica in its many forms, with the major emphasis on quartz. Sosman studied in detail the many measurements of each property presented in the literature and studied in his own lab. He points out errors and omissions of each researcher, and attempts to arrive at a "best" value for each constant of quartz. Hence, Sosman was used as the primary resource for this presentation.

There are many interesting historical notes included in the references, too numerous to include here; but one observation made by Dr. Virgil Bottom emphasizes the historical contribution made by Pierre Curie, the "Father of Piezoelectricity": "It is remarkable, therefore, that the Curies were able to obtain a value for d_{11} in quartz which is only about 7% below the best value known today. Between 1880 and 1970, no fewer than thirty independent measurements of d_{11} in quartz have been reported and half of these values are further from the value commonly accepted today than that given by the Curies in 1880." Dr. Bottom goes on to conclude that, "... it may truthfully be said of Pierre Curie that he laid the cornerstone of modern electronic communication." [6]

The constants presented in Table I are not represented to be "The" constants, or "the best" constants, but only "good" constants—for the reasons outlined above. "The" constant only exists for a given piece of quartz of a given design. Change the design and some of the measurable constants will change. Use another piece of quartz from the same autoclave or the same vug (a cavity in which the crystals grow in nature) and the constants will change (at least to within the precision allowed by modern "state-of-the-art" measurement techniques).

No attempts have been made to "improve" upon these constants by curvefitting several sets of data, or by re-calculation. The only modification has been to convert a few constants to the same units of measurement. Where this has been done, the conversion constant is noted.

The temperature at which a measurement was made is indicated, if available. When no temperature is noted, the measurement was probably made at room temperature.

No representation is made as to completeness, accuracy, or appropriateness of any constant. Indeed, only a few of the constants found in the literature noted the error band of the values given; hence, allowing for the small differences between different sources, no error bands are indicated in Table I.

The author would appreciate receiving suggestions for the inclusion of other constants, or new or better values for the ones presented, with the intent of publishing a new list from time to time as data warrants. This is the second update of the original 1984 paper. Thanks to everyone who pointed out errors and omissions in the previous edition. Such suggestions may be sent to the author at the address above.

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TABLE I
"GOOD" FUNDAMENTAL MATERIAL CONSTANTS FOR CRYSTALLINE QUARTZ

CONSTANT NAME	VALUE	REFERENCE
ACCOUSTIC ATTENUATION	SEE REFERENCE	LAMB [21]
AXIAL RATIO c/a	1.1015 @ -250°C 1.1014 -200 1.1009 -100 1.1003 0 1.0996 100 1.0988 200 1.0979 300 1.0960 400 1.0956 500 1.0946 550 1.0940 573 1.09997 ? 1.100 20 1.10013 25	SOSMAN [1] p. 205, 368-370. SEE ALSO FRONDEL [7] P. 7,20,39 HEISING [8] P.103 CADY [9] P. 27 BRICE [18]
***** TEMPERATURE COEFFICIENT	***** -6.14X10 ⁻⁶ /°C @ 0°C	***** FRONDEL P. 39 SOSMAN P. 377
COMPOSITION	SILICON 46.72% OXYGEN 53.28% BY WEIGHT	SOSMAN P. 22,27
COMPRESSIBILITY COEFFICIENT VOLUME, (TRUE)	2.76X10 ⁻⁶ /kg/cm ² @ 0 kg/cm ² 2.65 2039 2.53 4079 2.42 6118 2.33 8157 2.25 10197 2.18 12236 NOTE: 1 megabarye=10 ⁶ dyne/cm ² = 1.1097 kg/cm ²	SOSMAN P.427. SEE ALSO P. 426- 433
CONDUCTIVITY, THERMAL	<u>PARALLEL</u> <u>PERPENDICULAR</u> <u>TEMP</u> -- 0.68 -252°C 0.117 0.0586 -190 0.0476 0.02409 - 78 0.0325 0.01731 0 0.0215 0.01333 100 0.029 0.016 20 cal/cm/s/°C	SOSMAN P. 419,420 FRONDEL P. 116
CURIE TEMPERATURE (ALSO KNOWN AS LOW-HIGH INVERSION, ALPHA-BETA INVERSION)	573.3°C (ON HEATING)	SOSMAN P. 116-125 FRONDEL P. 3, 117 CADY P. 31
KEY		PRIMARY REFERENCE SECONDARY REFERENCE

TABLE I, CONT.

CONSTANT NAME	VALUE	REFERENCE
DENSITY, ABSOLUTE	2.65067 g/cm ³ @ 0°C 2.64822 25 2.665 g/cm ³ @ -250°C 2.664 -200 2.659 -100 2.651 0 2.641 100 2.630 200 2.616 300 2.601 400 2.581 500 2.554 573	FRONDEL P. 114 CADY P. 412 SOSMAN P. 361 (ALSO P. 291-295)
***** TEMPERATURE COEFFICIENT, TRUE	***** 12x10 ⁻⁶ /°C @ -200°C 25.2 -100 33.6 0 40.0 100 46.6 200 54.9 300 67.4 400 100 500 141 550 *****	***** SOSMAN P.291, 362, 366 SEE ALSO FRONDEL P.114
***** TEMPERATURE COEFFICIENTS	***** T ¹ = -34.92X10 ⁻⁶ /°C T ² = -15.9X10 ⁻⁹ /°C ² T ³ = 5.30X10 ⁻¹² /°C ³ (APPARENTLY REFERENCED TO 25°C) *****	***** BECHMANN [5] SEE ALSO CADY P. 412
DIELECTRIC CONSTANT	4.6 PARALLEL TO Z-AXIS 4.60 4.5 PERPENDICULAR TO Z-AXIS 4.51 ***** e ₁₁ ^T = e ₂₂ ^T = 39.97X10 ⁻¹² F/m e ₁₁ ^S - e ₁₁ ^T = -0.76 e ₃₃ ^T = 41.03 e ₃₃ ^S - e ₃₃ ^T = 0 *****	SOSMAN P. 515 BOTTOM [10] SOSMAN BOTTOM SEE ALSO CADY P.414 FRONDEL P. 116 ***** BECHMANN
***** TEMPERATURE COEFFICIENT	***** PARALLEL: K=4.926[1-1.10X10 ⁻³ (T-10)- 2.4X10 ⁻⁵ (T-10) ²] PERPENDICULAR: K=4.766[1-9.9X10 ⁻⁴ (T-10)] FOR T=10 TO 31°C *****	***** SOSMAN P. 523 AND GRAPH P. 524
***** FIELD STRENGTH COEFFICIENT	***** K=0 TO 2,000 V/cm (PARALLEL) K=0 TO 12,000 V/cm (PERPENDICULAR) *****	***** CADY P. 415

TABLE I, CONT.

CONSTANT NAME	VALUE	REFERENCE
ELASTIC COEFFICIENTS THIRD ORDER	$c_{111} = -2.10 \times 10^{12} \text{ dyn/cm}^2$ $c_{112} = -3.45$ $c_{113} = +0.12$ $c_{114} = -1.63$ $c_{123} = -2.94$ $c_{124} = -0.15$ $c_{133} = -3.12$ $c_{134} = +0.02$ $c_{144} = -1.34$ $c_{155} = -2.00$ $c_{222} = -3.32$ $c_{333} = -8.15$ $c_{344} = -1.10$ $c_{444} = -2.76$	THURSTON [11]
ELECTRIC STRENGTH	$4 \times 10^6 \text{ V/cm}$ @ -80°C 7 @ 60	CADY P. 413
ENTROPY OF TRANSITION	1.08 e.u.	CRC P. D-51
ENTROPY	0.166 cal/g/°C @ 25°C	CRC P. D-85
HARDNESS, PENETRATION (AUERBACH)	$30.8 \times 10^3 \text{ kg/cm}^2$ PARALLEL TO Z 22.9 PERPENDICULAR	SOSMAN P. 491
MHO	7	SOSMAN P. 494
SCRATCH	667 (CORUNDUM = 1000)	SOSMAN P. 494
HEAT CAPACITY, TRUE	$5.4 \times 10^{-3} \text{ cal/g}$ @ -250°C 41.0 @ -200 111.2 @ -100 166.4 @ 0 204.3 @ 100 232.7 @ 200 254.3 @ 300 270.0 @ 400 291.0 @ 500 340(?) @ 573 (IN 20°C grams)	SOSMAN P. 314, 331 (Note: The CRC [19] equation on P. D-51 does not agree with Sosman.)
HEAT OF SOLUTION	30.29 kg-cal/formula wt in 34.6% HF	SOSMAN P. 318
HEAT OF TRANSFORMATION, LATENT (LOW-->HIGH QUARTZ)	2.5 cal/g 0.15 kg-cal/formula wt	SOSMAN P. 312
LATTICE CONSTANT "a"	4.9035 Angstroms @ 18°C 4.903 ? 4.91331 25 4.90288 25 4.91267 25 4.9127 25 4.9134 25 CULTURED	SOSMAN P. 226 HEISING P. 103 FRONDEL P. 25 CADY P. 735 CADY BRICE [18] BRICE
MAGNETIC SUSCEPTIBILITY (VACUUM)	PARALLEL PERPENDICULAR TYPE -1.21×10^{-6} -1.20×10^{-6} VOLUME -0.45 -0.45 MASS	SOSMAN P. 576

TABLE I. CONT.

CONSTANT NAME	VALUE	REFERENCE
MAGNETO-OPTIC ROTATION (VERDET CONSTANT)	0.15866 min @ 2194.92 angstroms, 20°C 0.04617 3612.5 0.02750 4678.15 0.02257 5085.82 0.01664 5892.9 0.01368 6438.47	SOSMAN P. 776
***** TEMPERATURE COEFFICIENT	w = w ₂₀ [1 + 0.00011(T - 20)] FOR T = 20 TO 100°C	***** SOSMAN P. 777
MELTING POINT	<1670°C 1710°C	FRONDEL P. 3 CRC P. D-201
PENETRATION, MODULUS OF	<u>PARALLEL</u> <u>PERPENDICULAR</u> 1062 kg/cm ² 859 kg/cm ²	SOSMAN P. 465
PIEZOELECTRIC COEFFICIENTS	<u>STRAIN</u> d ₁₁ = -2.30X10 ⁻¹² m/V d ₁₁ = -2.27 d ₁₁ = -2.25 d ₁₁ = -2.30 d ₁₄ = 0.57X10 ⁻¹² m/V d ₁₄ = 0.85 d ₁₄ = 0.67 NOTE: 1 esu/dyne = 3 X 10 ⁴ m/V d ₁₁ = 2.32 X 10 ⁻¹² m/V @ 1.5°K 2.32 4.2 2.31 -196 °C 2.22 20 2.05 100 <u>STRESS</u> e ₁₁ = 0.171C/m ² e ₁₁ = 0.180 e ₁₄ = 0.0403 e ₁₄ = 0.04	SOSMAN P. 559 BOTTOM [12] HEISING P. 20 CADY P. 219 SOSMAN HEISING CADY GRAHAM [13] BECHMANN CADY P. 219, 224 BECHMANN CADY
***** PRESSURE COEFFICIENT	d ₁₁ Varies by <0.1% to 3519 kg/cm ²	***** SOSMAN P. 559
POISSON'S RATIO	S ₁₂ /S ₁₁ = 0.130 S ₁₃ /S ₁₁ = 0.119	CADY P. 156
RESISTIVITY	<u>PARALLEL</u> <u>PERPENDICULAR</u> <u>TEMPERATURE</u> 0.1 X 10 ¹⁵ 20 X 10 ¹⁵ 20°C 0.8 X 10 ¹² 100 70 X 10 ⁹ 200 60 X 10 ⁶ 300 ohm-cm	SOSMAN P. 528-537 ALSO SEE KOLODIEVA[14]-and JAIN & NOWICK [17]

TABLE I, CONT.

CONSTANT NAME	VALUE	REFERENCE
<p>REFRACTIVE INDEX</p> <p>*****</p> <p>TEMPERATURE COEFFICIENTS</p> <p>*****</p> <p>BIREFRINGENCE, TEMPERATURE COEFFICIENT</p>	<p><u>ORDINARY RAY:</u></p> $n_o^2 = 3.4269 + 1.0654 \times 10^{-2} / (L^2 - 0.010627) + 111.49 / (L^2 - 100.77)$ <p><u>ORDINARY RAY:</u></p> $n_o^2 = 3.53445 + 0.008067 / (L^2 - 0.0127493) + 0.002682 / (L^2 - 0.000974) + 27.2 / (L^2 - 108)$ <p><u>EXTRAORDINARY RAY:</u></p> $n_e^2 = 3.5612557 + 0.00844614 / (L^2 - 0.0127493) + 0.00276113 / (L^2 - 0.000974) + 127.2 / (L^2 - 108)$ <p>where L = wavelength in μ</p> <p>$n_o = 1.54425$ (Na @ 18°C) $n_e = 1.55336$</p> <p>*****</p> <p>ORDINARY RAY: $-6.50 \times 10^{-6} / ^\circ\text{C}$ EXTRAORDINARY RAY: -7.544</p> <p>*****</p> <p>$B = B_o - (972T + 1.6T^2) \times 10^{-9}$ FOR T = 4 TO 99°C</p>	<p>SOSMAN P. 588-625</p> <p>FRONDEL P. 129</p> <p>FRONDEL</p> <p>CADY P. 723</p> <p>*****</p> <p>FRONDEL P. 129, SOSMAN P. 637</p> <p>*****</p> <p>SOSMAN P. 684, FRONDEL P. 131</p>
<p>ROTARY POWER</p> <p>*****</p> <p>TEMPERATURE COEFFICIENT</p>	<p>201.9°/mm @ 2265.03 angstroms 95.02 3034.12 21.724 5892.9 11.589 7947.63 0.972 25000</p> <p>ROTATION IS CW IN RIGHT HAND QUARTZ AND CCW IN LEFT HAND QUARTZ.</p> <p>*****</p> <p>about $+1.4 \times 10^{-4} / ^\circ\text{C}$ at 20°C (independent of wavelength)</p>	<p>SOSMAN P. 648 FRONDEL P. 132</p> <p>*****</p> <p>SOSMAN P. 689</p>
<p>SPECIFIC HEAT</p>	<p>0.1412 cal/g/°C @ -50°C 0.1664 0 0.1870 50 0.2043 100</p>	<p>CADY P. 411</p>

TABLE I, CONT.

CONSTANT NAME	VALUE			REFERENCE	
STIFFNESSES	c^D		c^E	BECHMANN SEE ALSO HEISING P.40ff SOSMAN p. 463, CADY P.137-155 (GRAPHS) ALSO CADY P. 757	
	$c_{11} = 87.49$		$86.74 \times 10^9 \text{N/m}^2$		
	$c_{13} = 11.91$		11.91		
	$c_{33} = 107.2$		107.2		
	$c_{14} = -18.09$		-17.91		
	$c_{44} = 57.98$		57.94		
	$c_{66} = 40.63$		39.88		
***** TEMPERATURE COEFFICIENTS	*****			*****	
	FIRST $ij \times 10^{-6}/^\circ\text{C}$	SECOND $\times 10^{-9}/^\circ\text{C}^2$	THIRD $\times 10^{-12}/^\circ\text{C}^3$		
	11 -48.5 -49.6	-107 -107	-70 -74	BECHMANN [5] ADAMS [4] SEE ALSO HEISING P. 55, CADY P. 136-140, KOSINSKI [20]	
	13 -550 -651	-1150 -1021	-750 -240		
	33 -160 -192	- 275 -162	-250 67		
	14 101 89	-48 -19	-590 -521		
	44 -177 -172	-216 -261	-216 -194		
	66 178 167	118 164	21 29		
STRENGTH	STRENGTH	CONFINING PRESS	TEMP		
COMPRESSIVE	24,000kg/cm ² 150,000	1 atm 25,000 atm	20°C 400		FRONDEL P. 109
***** COMPRESSIVE	***** 24,500 kg/cm ² 22,400	***** PARALLEL PERPENDICULAR	*****		***** SOSMAN P. 481 SEE ALSO SCHOLZ [15]
TENSILE	1,120 850	PARALLEL PERPENDICULAR			
RUPTURE (BENDING)	1,380 920	PARALLEL PERPENDICULAR			
SYMMETRY	TRIGONAL TRAPEZOHEDRAL or TRIGONAL ENANTIOMORPHOUS HEMIHEDRAL			SOSMAN P. 183	
	TRIGONAL HOLOAXIAL or ENANTIOMORPHOUS HEMIHEDRAL			CADY P. 19	
***** CLASS	***** CLASS 18, SYMMETRY D_3 (SCHONFLIES) SYMMETRY 32 (HERMANN-MAUGUIN)			***** CADY P. 19	

TABLE I, CONT.

CONSTANT NAME	VALUE			REFERENCE		
THERMAL EXPANSION COEFFICIENT, LINEAR (MEAN, FROM 0°C)	<u>PARALLEL</u>	<u>PERPENDICULAR</u>	<u>TEMPERATURE</u>	SOSMAN P. 370		
	4.10X10 ⁻⁶ /°C	8.60X10 ⁻⁶ /°C	-250°C			
	5.50	9.90	-200			
	6.08	11.82	-100			
	7.10	13.24	0			
	7.97	14.45	100			
	8.75	15.61	200			
	9.60	16.89	300			
	10.65	18.50	400			
	12.22	20.91	500			
	15.00	25.15	573			
	*****	*****	*****		*****	
	TEMPERATURE COEFFICIENTS	<u>FIRST</u>	<u>SECOND</u>		<u>THIRD</u>	BECHMANN KOSINSKI[20]
	ij	X10 ⁻⁶ /°C	X10 ⁻⁹ /°C ²		X10 ⁻¹² /°C ³	
	11	13.71	6.5		-1.9	
33	7.48	2.9	-1.5			
NOTE: a ₁₁ = a ₂₂						
THERMOELASTIC COEFFICIENTS (HIGHER ORDER)	ORDER	a ₁₁ ⁽ⁿ⁾	a ₃₃ ⁽ⁿ⁾	UNIT	BALLATO [16]	
	1	13.16	6.37	10 ⁻⁶ /°C		
	2	15.68	8.18	10 ⁻⁹ /°C ²		
	3	-7.86	6.88	10 ⁻¹² /°C ³		
	REFERENCED TO 0°C					
WAVELENGTH, X-RAY Cu Kα ₁	1.5374 angstroms 1.54051			HEISING P. 97 FRONDEL P. 25		
VOLUME, UNIT CELL	37.40X10 ⁻²⁴ cm ³			SOSMAN P. 225		
YOUNG'S MODULUS	1.03X10 ⁺¹² dynes/cm ² PARALLEL 0.78 PERPENDICULAR S' ₃₃ X10 ¹⁵ = 1269 - 841 cos ² θ + 543 cos ⁴ θ -862 sin ³ θ cosθ sin ³ φ cm ² /dyne NOTE: Y _m = 1/s' ₃₃			CADY P. 155 (GRAPH) FRONDEL P. 122-CORRECTED (NOTE: EQ. IN FRONDEL HAS EXTRA TERM DUE TO TYPO AND INCORRECT POWER OF 10)		
VAPOR PRESSURE	10mm @ 1732°C 40 1867 100 1969 400 2141 760 2227			CRC P. D-201		
VISCOSITY	SEE REFERENCE			LAMB [21]		
	KEY			PRIMARY REFERENCE SECONDARY REFERENCE		

NOTE: PARALLEL = PARALLEL TO Z-AXIS (OPTICAL AXIS)
PERPENDICULAR = PERPENDICULAR TO Z-AXIS