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THE STATE OF VERIFICATION OF THE NONLINEAR ELECTROMECHANICAL CONSTANTS OF QUARTZ [1]

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This paper presents the results of an attempt to verify the third-order nonlinear electromechanical constants of α-quartz by direct comparison of their values which can be obtained independently from different experiments. Using this method and the criteria adopted it appears that only 5 pairs of the values have been found in agreement while 7 pairs are significantly different. None of the 31 fundamental nonlinear constants has been satisfactorily verified.

I. INTRODUCTION

The investigation of the third-order nonlinear electromechanical constants of α-quartz is well advanced. Attempts have been made to determine the value of all of them, in a number cases more than once. The time has come to be concerned with the consistency of the results and their verification.

There can be no doubt that the best method to verify the nonlinear constants is based on a direct comparison of their values obtained by different experimental methods. This paper shows the results which have been thus obtained.

All nonlinear material constants appearing in this paper are related to the state of a constant zero strain and zero electric field. Their numerical values are stated for right-hand quartz and the frame of reference according to the IEEE Standard 176 of 1978 [1] and for room temperature.

II. METHOD

There exist 31 third-order nonlinear electromechanical constants of quartz. They include eight electroelastic constants

$$f_{111},\ f_{113},\ f_{114},\ f_{122},\ f_{124},\ f_{134},\ f_{144},\ f_{315}, \qquad (1)$$

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eight electrostrictive constants

$$l_{11},\, l_{12},\, l_{13},\, l_{14},\, l_{31},\, l_{33},\, l_{41},\, l_{44}, \tag{2}$$

one third-order dielectric constant

$$\kappa_{111}, \tag{3}$$

and fourteen third-order elastic constants

$$\begin{gathered} c_{111},\, c_{112},\, c_{113},\, c_{114},\, c_{123},\, c_{124},\, c_{133} \\ c_{134},\, c_{144},\, c_{155},\, c_{222},\, c_{333},\, c_{344},\, c_{444}. \end{gathered} \tag{4}$$

The above fundamental nonlinear constants are studied by means of various experiments [2, 3, 4, 5]. Past experience indicates that the theoretical relationship of individual observations of a suitable experimental quantity to the nonlinear constants can be recorded using linear equations.

To minimize the effect of the experimental errors, the number of observations is made as large as possible. It is always larger than the number of unknown nonlinear constants to be determined. A linear system is thus obtained; as a result of the experimental errors it is overdetermined. The values of the unknown nonlinear constants are sought from the overdetermined system using a data reduction process called the least-squares fit. It provides the best estimates of the values of the nonlinear constants and their standard errors.

No experiment is known to produce the complete set of 31 values of the above nonlinear constants; different experiments produce only its subsets which are typically partly overlapping. The subsets generally consist of individual fundamental constants (1)-(4) or their linear combinations. Together they are referred to as the nonlinear parameters.

The verification of the nonlinear constants made in this paper is based on a comparison of the nonlinear parameters which are obtained from different experiments and which are dependent exclusively on these experiments. During the verification process the following *ad hoc* rules are used:

(a) Two parameter values are said to be in agreement if the absolute value of their difference is smaller than the standard error of the difference.

(b) If the absolute value of the difference is three times larger than its standard error, the parameter values are regarded as significantly different.

(c) If the values of the parameters produced by two different experiments are all simultaneously in agreement, then their values will be considered (mutually) verified.

The requirement that the agreement be reached simultaneously for all parameters being compared is probably quite restrictive. It serves as a precaution against the risk involved in accepting some of the parameters values as verified while other, simultaneously computed values are still at variance. If some of the parameter values are not in agreement, then improvements in the experiments or their theory will be sought to remove the discrepancies. It is difficult to say how such changes may affect the values of the parameters which were in agreement before the changes were made. It is important to make sure that they remain in agreement before they are accepted as verified.

Table 1

Independently calculable nonlinear parameters of α-quartz.

k_{111}	$= f_{111}$	$+2.310.10^{-12}c_{111}$	$-2.310.10^{-12}c_{112}$	$-0.727.10^{-12}c_{114}$
k_{113}	$= f_{113}$	$+2.310.10^{-12}c_{113}$	$-2.310.10^{-12}c_{123}$	$-0.727.10^{-12}c_{134}$
k_{114}	$= f_{114}$	$+2.310.10^{-12}c_{114}$	$-2.310.10^{-12}c_{124}$	$-0.727.10^{-12}c_{144}$
k_{122}	$= f_{122}$	$+2.310.10^{-12}c_{111}$	$+2.310.10^{-12}c_{112}$	$+0.727.10^{-12}c_{114}$
		$+1.454.10^{-12}c_{124}$	$-4.620.10^{-12}c_{222}$	
k_{124}	$= f_{124}$	$+2.310.10^{-12}c_{114}$	$+6.930.10^{-12}c_{124}$	$-0.727.10^{-12}c_{155}$
k_{134}	$= f_{134}$	$+4.620.10^{-12}c_{134}$	$-0.727.10^{-12}c_{344}$	
k_{144}	$= f_{144}$	$+2.310.10^{-12}c_{144}$	$-2.310.10^{-12}c_{155}$	$-0.727.10^{-12}c_{444}$
k_{315}	$= f_{315}$			
k_{11}	$= l_{11}$	$+1.205.10^{-12}c_{111}$	$-0.603.10^{-12}c_{112}$	$-0.379.10^{-12}c_{114}$
		$+0.379.10^{-12}c_{124}$	$+0.060.10^{-12}c_{144}$	$-0.603.10^{-12}c_{222}$
k_{13}	$= l_{13}$	$+2.00\ l_{44}$	$+1.205.10^{-12}c_{113}$	$-1.205.10^{-12}c_{123}$
		$-0.759.10^{-12}c_{134}$	$+0.060.10^{-12}c_{344}$	
k_{14}	$= l_{14}$	$-2.411.10^{-12}c_{124}$	$-0.379.10^{-12}c_{144}$	$+0.379.10^{-12}c_{155}$
		$+0.060.10^{-12}c_{444}$		
k_{31}	$= l_{31}$	$+2.00\ l_{44}$		
k_{33}	$= l_{33}$			
k_{41}	$= l_{41}$			
q_{111}	$= \kappa_{111}$	$-2.045.10^{-23}l_{12}$	$-2.465.10^{-35}c_{111}$	$+1.233.10^{-35}c_{112}$
		$+0.776.10^{-35}c_{114}$	$-2.329.10^{-35}c_{124}$	$-0.367.10^{-35}c_{144}$
		$+0.244.10^{-35}c_{155}$	$+1.234.10^{-35}c_{222}$	$+0.038.10^{-35}c_{444}$

The parameters are linear combination of the third-order nonlinear material constants c_{ijk} in N/m^2, electroelastic constants f_{ijk} in N/(Vm), electrostrictive constants l_{ij} (dimensionless) and third-order dielectric constant κ_{111} in F/V. Their values can be determined independently by the resonator method [2] and by the transit-time method [5] using dc field interactions.

III. RESULTS

Following the above rules a verification attempt can be made for the nonlinear parameters calculated independently from the data obtained by the resonator experiment [6, 7, 8, 9] and by the transit-time experiment [10]. Each of the data sets provides independently values of the 15 nonlinear parameters whose definitions are listed in Table 1. Three of them are isolated fundamental nonlinear constants; the rest are linear combinations of the fundamental constants.

The actual estimates of the parameters and their standard errors are stated in Table 2. The first two numerical columns contain the estimates as computed from the resonator and transit-time experiment data, respectively. They have been determined by the least-squares fit [11]. The last column represents the differences between the estimates and the associated standard errors.

Using the above stated criteria, the number of estimates which are found in

Table 2

Values of nonlinear parameters of α-quartz calculated independently from data obtained by resonator [6, 7, 8, 9] and transit-time [10] experiment.

parameter	resonator method	transit-time method	difference
k_{111}	2.38 ± 0.05	2.33 ± 0.06	0.05 ± 0.05
k_{113}	0.29 ± 0.07	0.17 ± 0.06	0.12 ± 0.07
k_{114}	0.63 ± 0.04	0.68 ± 0.04	-0.05 ± 0.04
k_{122}	-0.74 ± 0.03	-0.73 ± 0.05	-0.01 ± 0.03
k_{124}	1.38 ± 0.02	1.39 ± 0.02	0.01 ± 0.02
k_{134}	1.71 ± 0.03	1.71 ± 0.03	0.00 ± 0.03
k_{144}	-0.03 ± 0.03	0.04 ± 0.02	-0.07 ± 0.03
$k_{315} = f_{315}$	-0.79 ± 0.03	-0.89 ± 0.02	0.10 ± 0.03
k_{11}	-3.19 ± 0.91	4.92 ± 6.04	-8.11 ± 1.50
k_{13}	-8.62 ± 2.59	13.13 ± 3.75	-21.75 ± 2.65
k_{14}	-2.43 ± 0.54	-5.93 ± 2.54	3.50 ± 0.73
k_{31}	-12.40 ± 2.99	0.85 ± 3.18	-13.25 ± 3.00
$k_{33} = l_{33}$	-8.39 ± 6.79	-3.34 ± 4.39	-5.05 ± 6.71
$k_{41} = l_{41}$	-4.42 ± 0.67	-1.44 ± 2.21	-2.98 ± 0.79
$q_{111} \cdot 10^{20}$	-0.29 ± 0.24	3.72 ± 2.41	-4.01 ± 0.54

k_{ijk} are in N/(Vm), k_{ij} are dimensionless, q_{111} is in F/V. The last column represents the difference between the values in the preceding two columns. Only three of the parameters are the fundamental nonlinear constants (electroelastic constant f_{315}, and electrostrictive constants l_{33} and l_{41}). The errors are standard errors.

agreement is rather limited. It includes the estimates of parameters k_{111}, k_{122}, k_{124}, k_{134} and k_{33}. On the other hand there exist 7 parameters, k_{315}, k_{11}, k_{13}, k_{14}, k_{31}, k_{41} and q_{111}, whose estimates provided by the two methods are significantly different. As some of the parameter values are not in agreement, none of the values is accepted as verified.

IV. DISCUSSION

The method of verification of the nonlinear constans of quartz based on a comparison of independently obtained estimates is naturally limited to the instances where two or more estimates of the same nonlinear parameter are available. The parameters listed in Table 1 and 2 represent the current maximum number of such cases for the nonlinear constants discussed in this paper.

Using the suggested criteria, two independent estimates of a parameter can be found in agreement even though their values are strikingly different. Such is the case of parameter $k_{33} = l_{33}$ in Table 2. This is so because the standard errors of both estimates are quite large. On the other hand two numerically close estimates of the electroelastic constants f_{315} are in fact significantly different because their standard errors are very small.

Table 3

Current values of the nonlinear constants of α-quartz whose values have been determined by different methods.

nonlinear constant	transit-time	resonator method
f_{111}	2.14	2.18
f_{113}	-0.54	-0.42
f_{114}	0.24	0.19
f_{122}	-1.12	-1.14
f_{124}	0.76	0.76
f_{134}	1.64	1.64
f_{144}	0.09	0.02
f_{315}	-0.89±0.02	-0.79±0.03
l_{11}	4.83	-3.28
l_{14}	-5.89	-2.38
l_{33}	-3.34±4.39	-8.39±6.79
l_{41}	-1.44±2.21	-4.42±0.67
$\kappa_{111} \cdot 10^{20}$	3.71	0.060 *)

f_{ijk} are electroelastic constants in N/(Vm), l_{ij} are electrostrictive constants (dimensionless), κ_{111} is third-order dielectric constants in F/V. The errors are standard errors. Obtained by transit-time method [5] and resonator method [2]; the value marked *) is based on the *LC* oscillator method [14] and taken from [15]. The rest of the values given according to [11].

A question can be asked why the proposed verification method has not been applied more broadly to the individual fundamental nonlinear constants (1)-(4) rather than to their linear combinations. As regards the third-order elastic constants (4) the reason is quite simple. There exists only one set [12] of these constants so that no comparisons are possible. As regards the remaining three types of constants, i.e., the electroelastic constants (1), the electrostrictive constants (2) and the third-order dielectric constant (3), the reason lies elsewhere.

Table 3 shows that while the values of most of the constants (1)-(3) are known from two different sources, their standard errors are, for the most part, missing. Without the standard errors the degree of agreement between their values cannot be properly assessed.

The reason for the missing standard errors has been explained earlier [13]. It is associated with the fact that the afflicted estimates are not obtained from the indicated experiments independently. Their calculation requires that values of other nonlinear constants, determined by other experiments, be also used.

On the other hand, the estimates of the individual fundamental constants appearing in Table 3 which are provided with standard errors and, as such, can be compared have already been covered in Table 2.

V. CONCLUSION

The verification method for the nonlinear constants of α-quartz recommended and used in this paper is based on a direct comparision of the values of the fundamental nonlinear constants or their combinations obtained independently by different experiments.

The criteria of agreement and verification adopted are hoped to meet what would normally be expected of a set of rules to serve the declared purpose. Otherwise they have been chosen arbitrarily. If necessary, they can be modified at a later time.

There are 31 fundamental electromechanical constants of quartz defined at a constant (zero) strain and electric field which need to be verified. The current attempt to do so has to be limited to 15 cases only. For the most part, it involves linear combinations of these constants. Only 5 pairs of the compared values have passed the criterion of agreement. In the presence of a number of other, contradictory results, none of the values is regarded as verified.

Other verification methods of the nonlinear constants used in the past are based (a) on the quality of least-squares fit attained during the process of their calculation or (b) of the potential of the nonlinear constants to predict new experimental data. This paper does not reject these other verification methods. It only tries to avoid their weaknesses as outlined earlier [16].

Large discrepancies between the values of the nonlinear constants are still awaiting an explanation. Future effort should be directed towards an improved theory interpreting the experiments as well as further acquisition of data using experimental specimens designed to reduce the standard errors of the least-squares estimates of the nonlinear constants.

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