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NONLINEAR MATERIAL PROPERTIES OF QUARTZ DETERMINED BY THE RESONATOR METHOD

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Attempts to provide least-squares estimates of all 31 independent thrid-order nonlinear electromechanical constants of alpha quartz using the resonator method produce parameters containing third-order elastic constants linearly combined with the remaining three types of electromechanical nonlinearities: electroelastic, electrostrictive and dielectric.

To maximize the yield of the resonator method in terms of these latter three types of nonlinear constants, the third-order elastic constants must be "imported" from an external source. They can be introduced, with the same effect, before or after the least-squares process is executed. Their reliability is crucial for the quality of the electroelastic constants and apparently (considering the size of their respective standard errors) less important for the electrostrictive and third-order dielectric constants.

A comparison with the results of others, yielding in most cases an excellent agreement, is facilitated by introducing uniformity into the values of the linear constants used for their determination. This produces changes in the calculated nonlinear parameters but does not remove the few differences which were noted.

1. Introduction

Interactions between the dc electric field and alpha quartz provide valuable information about its material nonlinearities. One of the methods exploiting this principle is the resonator method. It is based on observations of the changes in the resonance frequency of quartz resonators induced by a dc electric field acting on the crystal material.

The current set of the experimental data provided by the resonator method has been used before (in part) e.g. by HRUSKA [7] and by HRUSKA and BRENDEL or (in total) by HRUSKA [8]. The last work resulted in the determination of the complete set electroelastic constants of quartz, several electrostrictive constants, some isolated and others in combination among themselves or with the (only) third-order permittivity of quartz.

In the process of all above applications of the resonator method the third-order elastic constants of quartz were employed which were determined much earlier by THURSTON, McSKIMMIN and ANDREATCH [18]. This was done so because the main thrust of the past work was directed towards the determination of other third-order material constants regarded as unknown or unverified. The third-order elastic constants were employed with little thought for whether or not it was actually necessary. The consequencies of this decision, in either case, have not been considered. To do so is the main objective of this work.

In the course of the work an attempt must be made to determine all four third-order electromechanical nonlinearities in quartz from the resonator method data. This produces results which are completely independent of all other nonlinear material constants determined earlier and invites a comparison with the results of others. In the past such comparisons were made without the benefit of assured independence of the compared quantities and, disregarding the fact that different authors use different sets of the linear material constants for their computation. In the comparisons made here this past omission is rectified.

The numerical values of all quantities (generated or referenced) in this paper are stated for right-hand quartz and its basic frame of reference according to the IEEE Standard 176 of 1978 [20].

2. Experimental data

The study of quartz nonlinearities made in this paper is done using the resonator method. It is based on observations of the linear coefficient L of the dependence of the resonance frequency f of quartz resonators on the dc electric field E applied to their body. This phenomenon has also been known as the polarizing effect or the electroelastic effect. The linear coefficient of the frequency–dc field dependence is defined as $L = (1/f)\cdot(df/dE)_{E=0}$.

The observations of the linear coefficient L used in this paper are the 184 values listed in [9]. They have been accumulated over a period of twenty years and originate from HRUSKA and KHOGALI [12], KINIGADNER [21], HRUSKA, MERIGOUX and KUCERA [13] and from HRUSKA and BRENDEL [11].

The observations of L were obtained for a variety of doubly rotated rectangular rods vibrating in length and plates vibrating in thickness. To describe their orientation an orthogonal frame of reference is used whose axes X'_1, X'_2 and X'_3 are fixedly connected with each resonator and parallel to its thickness t, width w and length l, respectively. This reference frame is related to the basic frame of reference X_1, X_2 and X_3 (denoted respectively X, Y, and Z in [20]) through the following matrix of the direction cosines

	X_1	X_2	X_3
X'_1	α_{11}	α_{12}	α_{13}
X'_2	α_{21}	α_{22}	α_{23}
X'_3	α_{31}	α_{32}	α_{33}.

The orientation of both the rods and the plates relative to the basic frame of reference is also stated in [9] and given using the IEEE rotational symbol $(XZlwt)\psi/\phi/\theta$ [20]. The values of the corresponding direction cosines α_{AB} which are needed later are fully calculable from the orientation angles ψ, ϕ and θ. The dc electric field E acting on the resonators is always in the direction of X'_1 (resonator thickness) related to the basic reference frame by the direction cosines α_{11}, α_{12}, α_{13}.

3. The model of the linear coefficient L

The model linking the observations of the linear coefficient L to the nonlinear material tensors of quartz is based on the nonlinear theory of dielectrics. Its most recent version described in [8] is recorded as follows

$$L = A_{MIJKL} \cdot f_{MIJKL} + B_{MNIJ} \cdot l_{MNIJ} + C_{MRS} \cdot \varkappa_{MRS} + D_{IJKLMN} \cdot c_{IJKLMN} + E. \tag{1}$$

It relies on the earlier results by BAUMHAUER and TIERSTEN [2], BRENDEL [5], TIERSTEN and BALLATO [19], KITTINGER and TICHY [14], HRUSKA and BRENDEL [11], HRUSKA [7], and HRUSKA and BRENDEL [10].

The model presents the linear coefficient L as a linear function of four third-order nonlinear material tensors: c_{IJKLMN}, the third-order elastic stiffness tensor; l_{MNIJ}, the total electrostrictive tensor; f_{MIJKL}, the electroelastic tensor; and $\varkappa_{MRS}$, the third-order dielectric permittivity tensor. The electrostrictive tensor l_{MNIJ} is defined according to NELSON [17] and consists of the relative electrostrictive tensor and the Maxwell vacuum electric-stress tensor (Eq. (54), [17]). All these tensors are defined in the basic frame of reference of quartz according to [20]. They are defined for zero strain and zero electric field in the crystal material.

The coefficients A_{MIJKL}, B_{MNIJ}, C_{MRS}, D_{IJKLMN}, and the absolute term E in Eq. (1) are functions of the known second-order (linear) material constants of quartz and of the resonator orientation and mode of vibration. Their definition given in [8] will be restated below.

All uppercase indices used above and throughout the paper take on the values of 1, 2, 3. The Einstein summation rule is in effect everywhere except where explicitly stated otherwise.

Two types of resonators and vibrations, thickness modes of plates and the extensional mode of rods, provide the experimental values of L used in this paper. The definitions of the coefficients A_{MIJKL}, B_{MNIJ}, C_{MRS}, D_{IJKLMN}, and the absolute term E in Eq. (1) need to be given for each type of resonator separately. For the rods they are

$$A_{MIJKL} = \frac{1}{2} F'_{AB} s'_{33CD} \alpha_{1M} \alpha_{AI} \alpha_{BJ} \alpha_{CK} \alpha_{DL}, \tag{2}$$

$$B_{MNIJ} = 0, \tag{3}$$

$$C_{MRS} = 0, \tag{4}$$

$$D_{IJKLMN} = \frac{1}{2} F'_{AB} s'_{33CD} d'_{1EF} \alpha_{AI} \alpha_{BJ} \alpha_{CK} \alpha_{DL} \alpha_{EM} \alpha_{FN}, \tag{5}$$

$$E = \frac{1}{2} F'_{AB} s'_{33CD} (c'_{FBCD} d'_{1AF} + c'_{FDAB} d'_{1CF}), \tag{6}$$

where

$$F'_{AB} = (2\delta_{3A} - \delta_{3A}\delta_{3B} + \delta_{2A}\delta_{2B} + \delta_{1A}\delta_{1B} + \delta_{2A}\delta_{1B} + \delta_{1A}\delta_{2B}) s'_{AB33}/s'_{3333}, \tag{7}$$

$$s'_{AB33} = s'_{33AB} = \alpha_{AI}\alpha_{BJ}\alpha_{3K}\alpha_{3L} s_{IJKL}, \tag{8}$$

$$s'_{3333} = \alpha_{3I}\alpha_{3J}\alpha_{3K}\alpha_{3L} s_{IJKL}, \tag{9}$$

$$d'_{1AB} = \alpha_{1I}\alpha_{AJ}\alpha_{BK} d_{IJK}. \tag{10}$$

In Eq. (7) the Einstein summation rule is not in effect for the indices A and B on the right hand side of the definition of F'_{AB}.

The expressions for the coefficient D_{IJKLMN} and for the absolute term E in Eqs. (5) and (6), respectively, do not appear in [8] explicitly. However, they are obtained from the absolute term C there (Eq. (7), [8]) after it is recorded as a linear function of the third-order elastic stiffness tensor components c_{IJKLMN}

$$C = D_{IJKLMN} \cdot c_{IJKLMN} + E. \tag{11}$$

The above definitions (4)–(10) contain some material tensor components the meaning of which has not been defined. They represent: s_{IJKL}, the tensor of the elastic compliances, and d_{IJK}, the piezoelectric strain tensor. They are both related to the basic frame of reference. δ_{MI} is the Kronecker delta.

The definitions of the coefficients A_{MIJKL}, B_{MNIJ}, C_{MRS}, D_{IJKLMN}, and of the absolute term E in Eq. (1) for the three thickness modes of vibration of plates are

$$A_{MIJKL} = (1/2\,\lambda)\alpha_{1M}(\alpha_{1I}\alpha_{1L} l_J l_K - 2r\alpha_{1J} l_I d_{RKL}), \tag{12}$$

$$B_{MNIJ} = (1/2\,\lambda)\varepsilon_0 \alpha_{1M}\alpha_{1N}(2r\alpha_{1J} l_I - r^2 \alpha_{1R} d_{RIJ}), \tag{13}$$

$$C_{MRS} = -(1/2\,\lambda) r^2 \alpha_{1M}\alpha_{1R}\alpha_{1S}, \tag{14}$$

$$D_{IJKLMN} = (1/2\,\lambda)\alpha_{1I}\alpha_{1L}\alpha_{1R} l_J l_K d_{RMN}, \tag{15}$$

$$\begin{aligned} E = (1/2\lambda)[\alpha_{1I}\alpha_{1E}(\alpha_{1J}\delta_{KM}\delta_{LN} + \alpha_{1L}\delta_{KN} l_J l_M \\ + \alpha_{1L}\delta_{JN} l_K l_M) d_{EMN} c_{IJKL} + \alpha_{1J}\alpha_{1L}(2r\alpha_{1R} l_I d_{RIK} - \alpha_{1K}) e_{JKL}], \end{aligned} \tag{16}$$

where

$$r = \alpha_{1I}\alpha_{1K} l_J e_{IJK}/(\alpha_{1A}\alpha_{1B}\varepsilon_{AB}). \tag{17}$$

The expressions for the coefficient D_{IJKLMN} and for the absolute term E in Eqs. (15) and (16), respectively, are obtained from the absolute term C (Eq. (11), [8]) after it is recorded as a linear function of the third-order elastic stiffness tensor components c_{IJKLMN} as done previously for the rods (Eq. (11)).

Again, all quantities on the right-hand side of Eqs. (12)–(17) are defined in the basic frame of reference. Those that have not yet appeared in this paper are explained now. They are: c_{IJKL}, the elastic stiffness tensor, e_{NIJ}, the piezoelectric stress tensor; and ε_{MN}, the dielectric permittivity tensor. The constant ε_0 is the permittivity of free space.

The quantity λ and the amplitude vector (l_1, l_2, l_3) of the plate vibrations in Eqs. (12)–(17) are the respective eigenvalue and eigenvector of the matrix

where $$(\Gamma_{IK}),$$

$$\Gamma_{IK} = \alpha_{1J}\alpha_{1L}c_{IJKL} + \alpha_{1N}\alpha_{1J}\alpha_{1M}\alpha_{1L}e_{NIJ}e_{MKL}/(\alpha_{1A}\alpha_{1B}\varepsilon_{AB}).$$

The three generally existing eigenvalue-eigenvector pairs of the above matrix correspond to the three thickness modes of vibrations of the plates under consideration.

4. Calculation of the nonlinearities

Returning to Eq. (1) and its preparation for the calculation of the third-order material constants of quartz, the upper case tensor indices there have been contracted to their lower case matrix form. The interchange symmetry among the uppercase indices and the symmetry of quartz have been taken into account and the conventional choice of the independent material constants made. Eq. (1) has taken on the form

$$\begin{aligned} L_i = {} & a_{i1}\cdot f_{111} + a_{i2}\cdot f_{113} + a_{i3}\cdot f_{114} + a_{i4}\cdot f_{122} \\ & + a_{i5}\cdot f_{124} + a_{i6}\cdot f_{134} + a_{i7}\cdot f_{144} + a_{i8}\cdot f_{315} \\ & + b_{i1}\cdot l_{11} + b_{i2}\cdot l_{12} + b_{i3}\cdot l_{13} + b_{i4}\cdot l_{14} \\ & + b_{i5}\cdot l_{31} + b_{i6}\cdot l_{33} + b_{i7}\cdot l_{41} + b_{i8}\cdot l_{44} \\ & + c_i\cdot \varkappa_{111} \\ & + d_{i1}\cdot c_{111} + d_{i2}\cdot c_{112} + d_{i3}\cdot c_{113} + d_{i3}\cdot c_{114} + d_{i5}\cdot c_{123} \\ & + d_{i6}\cdot c_{124} + d_{i7}\cdot c_{133} + d_{i8}\cdot c_{134} + d_{i9}\cdot c_{144} + d_{i10}\cdot c_{155} \\ & + d_{i11}\cdot c_{222} + d_{i12}\cdot c_{333} + d_{i13}\cdot c_{344} + d_{i14}\cdot c_{444} + E_i, \end{aligned} \tag{18}$$

where

$$f_{111}, f_{113}, f_{114}, f_{122}, f_{124}, f_{134}, f_{144}, f_{315} \tag{19}$$

are the eight independent electroelastic constants, and

$$l_{11}, l_{12}, l_{13}, l_{14}, l_{31}, l_{33}, l_{41}, l_{44} \tag{20}$$

are the eight independent electrostrictive constants, and

$$\varkappa_{111} \tag{21}$$

is the (only) independent third-order permittivity constant of quartz, and

$$c_{111}, c_{112}, c_{113}, c_{114}, c_{123}, c_{124}, c_{133},$$
$$c_{134}, c_{144}, c_{155}, c_{222}, c_{333}, c_{344}, c_{444} \tag{22}$$

are the third-order elastic constants of quartz.

The conversion of Eq. (1) to Eq. (18) is straightforward but tedious and, for these reasons, its details are not given in this paper. The index i has been added to various quantities in Eq. (18) in preparation for its application to all 184 observations of the linear coefficient denoted now L_i, $i = 1, 2, \ldots, 184$.

All thirty-one material constants (19)–(22) are the fundamental material constants of quartz related to its basic reference frame. In agreement with the tensors in Eq. (1) they are defined for zero strain and zero electric field in the crystal material.

Aiming at the determination of the nonlinear constants (19)–(22) Eq. (14) was applied to all observations of the linear coefficient L_i. Due to random errors in the experimental values of L_i, this led to an overdetermined linear system

$$\begin{aligned} L_i - E_i = {} & a_{i1}\cdot f_{111} + a_{i2}\cdot f_{113} + a_{i3}\cdot f_{114} + a_{i4}\cdot f_{122} \\ & + a_{i5}\cdot f_{124} + a_{i6}\cdot f_{134} + a_{i7}\cdot f_{144} + a_{i8}\cdot f_{315} \\ & + b_{i1}\cdot l_{11} + b_{i2}\cdot l_{12} + b_{i3}\cdot l_{13} + b_{i4}\cdot l_{14} \\ & + b_{i5}\cdot l_{31} + b_{i6}\cdot l_{33} + b_{i7}\cdot l_{41} + b_{i8}\cdot l_{44} \\ & + c_i\cdot \varkappa_{111} \\ & + d_{i1}\cdot c_{111} + d_{i2}\cdot c_{112} + d_{i3}\cdot c_{113} + d_{i3}\cdot c_{114} + d_{i5}\cdot c_{123} \\ & + d_{i6}\cdot c_{124} + d_{i7}\cdot c_{133} + d_{i8}\cdot c_{134} + d_{i9}\cdot c_{144} + d_{i10}\cdot c_{155} \\ & + d_{i11}\cdot c_{222} + d_{i12}\cdot c_{333} + d_{i13}\cdot c_{344} + d_{i14}\cdot c_{444}, \end{aligned} \tag{23}$$

where $i = 1, 2, \ldots, 184$.

The thirty-one material constants (19)–(22) were sought by a least-squares fit to this system. Prior to this a brief analysis of the system matrix and of the random errors of its left hand sides was necessary.

The matrix of linear system (23), to be referred to as M, consists of four concatenated matrices, a_{ij}, $(j = 1, 2, \ldots, 8)$, b_{ik}, $(k = 1, 2, \ldots, 8)$, c_i, and d_{il}, $(l = 1, 2, \ldots, 14)$. Applicability of the least-squares procedure requires that the elements of matrix M be known with total accuracy. As they are functions of the linear material constants of quartz as well as of the resonator orientations this requires a concession that they all be regarded as known without errors. This concession naturally extends to the absolute term E_i in Eq. (23) which is a function of the same quantities (Eqs. (6) and (16)).

The experimental values in the observed coefficients L_i are thus regarded to be the only source of random errors of the left hand sides of system (23). Subsequent analysis suggested that the measure of random errors in L_i are the variations in this quantity among resonators of identical orientation rather than the standard deviations of observations made for individual resonator units. It was not possible to estimate these variations for about one third of the observations of L_i in system (23) as some of the resonators were specimens of orientations dissimilar from other resonator used for this project. For this reason the least-squares procedure was executed using equal weighting of the left hand sides of system (23).

Two of the columns of matrix M, d_{i7} and d_{i12}, were found to be identically equal to zero. An additional fourteen columns, b_{i2}, b_{i8}, and d_{il}, $l = 1, 2, \ldots, 6, 8, 9, 10, 11, 13, 14$, were found to be linearly dependent on the remaining columns of matrix M. As a result the least-squares fit did not yield the values of all thirty-one sought constants (19)–(22) but rather only of fifteen parameters, most of them being linear combinations of these constants rather than their pure values.

The quality of the least-squares fit attained can be seen from the statistical indicators obtained during the least–squares process (MENDENHALL and SINCICH [22]): the sample multiple coefficient of determination $R^2 = 0.9976$ or the analysis of variance F test value = 4,707.

The values of the calculated parameters and their standard errors are placed in Table 1 and marked Solution 1. The definitions of the parameters in terms of the fundamental third-order material constants (19)–(22) are presented in Table 2.

Table 1. Third-order nonlinear material parameters and fundamental material constants of alpha quartz determined by the resonator method

	Solution 1 nonlinear parameters this work		Solution 2 nonlinear constants according to [8]
k_{111}	2.35 ± 0.05	f_{111}	2.16 ± 0.05
k_{113}	0.28 ± 0.07	f_{113}	-0.43 ± 0.07
k_{114}	0.60 ± 0.04	f_{114}	0.16 ± 0.04
k_{122}	-0.73 ± 0.03	f_{122}	-1.12 ± 0.03
k_{124}	1.37 ± 0.02	f_{124}	0.74 ± 0.02
k_{134}	1.72 ± 0.03	f_{134}	1.65 ± 0.03
k_{144}	-0.04 ± 0.03	f_{144}	0.01 ± 0.03
k_{315}	-0.78 ± 0.03	f_{315}	-0.78 ± 0.03
k_{11}	-3.0 ± 0.9	l_{11}	-3.1 ± 0.9
k_{13}	-8.7 ± 2.6	$l_{13} + 2.000\, l_{44}$	-9.1 ± 2.6
k_{14}	-2.4 ± 0.6	l_{14}	-2.3 ± 0.6
k_{31}	-11.2 ± 3.0	$l_{31} + 2.000\, l_{44}$	-11.2 ± 3.0
k_{33}	-7.7 ± 6.9	l_{33}	-7.7 ± 6.9
k_{41}	-4.7 ± 0.7	l_{41}	-4.7 ± 0.7
q_{111}	$(-2.4 \pm 2.5) \cdot 10^{-21}$	$\varkappa_{111} - 2.045 \cdot 10^{-23}\, l_{12}$	$(-2.4 \pm 2.5) \cdot 10^{-21}$

Parameters k_{ijk} and electroelastic constants f_{ijk} are in N/(V.m), parameters k_{ij} and electrostrictive constants l_{ij} are dimensionless, parameter q_{111} and third-order permittivity constant $\varkappa_{111}$ are in F/V. The numerical coefficient $2.045 \cdot 10^{-23}$ at l_{12} is also in F/V. The errors are standard errors. Given for room temperature, right-hand quartz and the frame of reference according to [20]. Solution 1 can be converted into Solution 2 using Table 2 and the third-order elastic constants according to [18]. Both solutions are calculated using the linear material constants of quartz taken from [3].

Table 2. Definition of third-order nonlinear material parameters of alpha quartz calculable by the resonator method

$$
\begin{aligned}
k_{111} &= f_{111} + 2.310\cdot 10^{-12} c_{111} - 2.310\cdot 10^{-12} c_{112} - 0.727\cdot 10^{-12} c_{114} \\
k_{113} &= f_{113} + 2.310\cdot 10^{-12} c_{113} - 2.310\cdot 10^{-12} c_{123} - 0.727\cdot 10^{-12} c_{134} \\
k_{114} &= \mathrm{f}_{114} + 2.310\cdot 10^{-12} c_{114} - 2.310\cdot 10^{-12} c_{124} - 0.727\cdot 10^{-12} c_{144} \\
k_{122} &= f_{122} + 2.310\cdot 10^{-12} c_{111} + 2.310\cdot 10^{-12} c_{112} + 0.727\cdot 10^{-12} c_{114} \\
&\quad + 1.454\cdot 10^{-12} c_{124} - 4.620\cdot 10^{-12} c_{222} \\
k_{124} &= f_{124} + 2.310\cdot 10^{-12} c_{114} + 6.930\cdot 10^{-12} c_{124} - 0.727\cdot 10^{-12} c_{155} \\
k_{134} &= f_{134} + 4.620\cdot 10^{-12} c_{134} - 0.727\cdot 10^{-12} c_{344} \\
k_{144} &= f_{144} + 2.310\cdot 10^{-12} c_{144} - 2.310\cdot 10^{-12} c_{155} - 0.727\cdot 10^{-12} c_{444} \\
k_{315} &= f_{315} \\
k_{11} &= l_{11} + 1.205\cdot 10^{-12} c_{111} - 0.603\cdot 10^{-12} c_{112} - 0.379\cdot 10^{-12} c_{114} \\
&\quad + 0.379\cdot 10^{-12} c_{124} + 0.060\cdot 10^{-12} c_{144} - 0.603\cdot 10^{-12} c_{222} \\
k_{13} &= l_{13} + 2.00\, l_{44} + 1.205\cdot 10^{-12} c_{113} - 1.205\cdot 10^{-12} c_{123} \\
&\quad - 0.759\cdot 10^{-12} c_{134} + 0.060\cdot 10^{-12} c_{344} \\
k_{14} &= l_{14} - 2.411\cdot 10^{-12} c_{124} - 0.379\cdot 10^{-12} c_{144} + 0.379\cdot 10^{-12} c_{155} \\
&\quad + 0.060\cdot 10^{-12} c_{444} \\
k_{31} &= l_{31} + 2.00\, l_{44} \\
k_{33} &= l_{33} \\
k_{41} &= l_{41} \\
q_{111} &= \varkappa_{111} - 2.045\cdot 10^{-23} l_{12} - 2.464\cdot 10^{-35} c_{111} + 1.233\cdot 10^{-35} c_{112} \\
&\quad + 0.777\cdot 10^{-35} c_{114} - 2.326\cdot 10^{-35} c_{124} - 0.367\cdot 10^{-35} c_{144} \\
&\quad + 0.244\cdot 10^{-35} c_{155} + 1.232\cdot 10^{-35} c_{222} + 0.038\cdot 10^{-35} c_{444}
\end{aligned}
$$

The parameters are combinations of the third-order nonlinear material constants of quartz including electroelastic constants f_{ijk}, third-order elastic constants c_{ijk}, electrostrictive constants l_{ij} and third-order permittivity $\varkappa_{111}$. The first eight parameters (k_{ijk}) are in N/(V.m), the next six (k_{ij}) are dimensionless, the last parameter (q_{111}) is in F/V. The numerical coefficients at c_{ijk} in parameters k_{ijk}, k_{ij} and q_{111} are in m^2/V, m^2/N and Fm^2/NV, respectively. The numerical coefficient at l_{12} in q_{111} is in F/V. The remaining numerical coefficients are dimensionless. The number and choice of indices of k_{ijk}, k_{ij} and q_{111} correspond to the first material constant in their definition.

The experimental values of the linear coefficient L and the linear material constants of quartz – the latter taken from BECHMANN [3] – needed in the above calculation are a mixture of quantities determined at 20 or 25°C. Consequently, the values of the nonlinear parameters in Table 1 are understood as valid for room temperature. Considering their existing accuracy (standard errors in Table 1) and their estimated temperature dependence [6] the temperature inconsistency of several degress Celsius is of no practical consequence. Similarly disregarded is the somewhat uncertain and probably nonuniform thermodynamic character of these quantitites which is not necessarily purely adiabatic.

A detailed numerical inspection of the solved system (23) has indicated that the standard errors in the individual parameters are commensurate with the standard errors in the experimental values of L (typically $\pm 0.26\cdot 10^{-12}$ m/V). Large relative errors occur in the case of those parameters whose contribution to the measured quantity L is relatively small.

The above comments concerning the thermodynamic character of the results and their standard errors apply to the entire contents of Table 1 with the meaning of Solution 2 yet to be explained.

5. Discussion

One of the principal ideas which inspired this work was a desire to produce values of the third-order nonlinear material constants of quartz exclusively by means of the resonator method and completely independent of any other third-order constants determined earlier or by other methods. It was hoped that among the result would also be the third-order elastic constants. They were intended for an independent verification of their old and only existing values [18] which were never tested in a similar direct manner. However, in spite of abundance of experimental data, the linear system (23) failed to produce a single isolated value of these material constants. It appears that the third-order elastic constants will not be put to test using the present data provided by the resonator method.

The same linear system (23) was solved once before [8]. At that time the values of the third-order elastic constants were substituted into it from [18] and the least-squares procedure applied only to the remaining third-order constants. The solution obtained there is restated in the second part of Table 1 and marked Solution 2.

It is a direct consequence of the multicolinearity detected in the system matrix M that the two solutions in Table 1 are very simply interrelated. Solution 2 can be obtained from Solution 1 if the latter is stripped of the contribution of the third-order elastic constants defined in Table 2 using the values of the third-order elastic constants [18].

When Solution 2 was computed with the aid of the third-order elastic constants taken from [18] it was clear that it would depend, for its quality, on the reliability of the old third-order elastic constants [18]. The existing relationship between Solution 1 and Solution 2 makes it possible to estimate their potential distortive effect. As a function of these constants, the distortion would be a portion of the difference between the corresponding parts of Solution 1 and Solution 2; in relative terms it would be probably larger for the electroelastic constants f_{113} or f_{114} and smaller for the electrostrictive constants l_{11} or l_{14}, and definitely zero for the constants f_{315}, l_{33}, l_{41} and for the combination $l_{31}+2l_{44}$. At the same time, however, it is appropriate to say that there seems to be no evidence available indicating that the existing values of the third-order elastic constants are in any way compromised.

At the time when Solution 1 was sought, the principal objective was the determination of the electroelastic constants of quartz. The decision to use the "imported" values of the third-order elastic constants in the process was a natural one – these constants were already available – and the matter was not given much further thought.

However, had the linear system (23) been able to provide its own values for the third-order elastic constants, then Solution 1 would not have been so simply related to (i.e. not directly convertible into) Solution 2. Depending on the difference between the imported third-order elastic constants and those provided by system (23) itself, the two solutions could have been in serious conflict and the question of using the values of third-order elastic constants external to the system (23) would have deserved much more attention.

It is only the result of this paper, namely the detected multicolinearity of the system matrix M, which provides a belated but vital reason to conclude that in trying to find the material constants determined in [8] it is impossible to do without the imported third-order elastic constants and that their use creates no conflict. In this sense this work validates the procedure adopted in [8].

Comparing Solution 1 and 2 further on, it is no coincidence that the standard errors for the two sets of quantitites are identical. Their interpretation requires an brief remark. First and foremost the stated standard errors apply to Solution 1, i.e. to the determined parameters k_{111} etc. Only if it is assumed that the third-order elastic constants from [18] are absolutely accurate, then the standard errors may be viewed as truly pertaining to quantites forming Solution 2, i.e. to the material constants f_{111} etc.

The results of this work are completely independent of all nonlinear material constants of quartz determined earlier or by other means. As such they are eminently suitable for comparisons with the results from other sources. This is of considerable interest not only for the sake of mutual verification of their immediate values but possibly also as a consistency test of the related applications of the nonlinear theory.

The comparison is made with a recent set of nonlinear constants listed by ADAM, TICHY and KITTINGER [1], whose values are taken over or derived from the work of BESSON and GAGNEPAIN [4], KITTINGER, TICHY and FRIEDEL [15] and THURSTON, MCSKIMMIN and ANDREATCH [18]. In preparation for the comparison, the values from [1] were substituted into the definitions of the parameters in Table 2. Substituting for the electroelastic constants f_{ijk} there, the third-order piezoelectric constants e_{ijk} from [1] were appropriately used with a reversed sign ($f_{ijk} = -e_{ijk}$). The results of the substitution were placed next to the results of this work into the last column of Table 3.

In most of the cases the differences between the results in Table 3 are comparable with the stated standard errors. This also seems to be the case with parameter q_{111}; however, the calculated standard error there is fairly large and the disagreement in sign is disturbing. On the other hand, there are parameters such as k_{13}, k_{31}, and, to a lesser degree, possibly others, which appear to be in conflict. Going just by the magnitude of their disagreement it is hard to classify it as insignificant.

On the whole the agreement in parameters k_{ijk} which are solely combinations of the third-order elastic and electroelastic constants appears to be better than that attained for the remaining parameters involving (apart from the third-order elastic constants) also electrostriction and third-order permittivity. This seems to agree well with the source of the current values of the electrostrictive constants [15] whose authors consider only one of their values as fairly reliable and advise caution regarding the rest of them.

Numerous comparisons between the nonlinear constants or their combinations

Table 3. Comparison of third-order nonlinear material parameters of alpha quartz obtained from independent sources

Nonlinear parameter	Resonator method this work	Other methods according to [1]
k_{111}	2.38 ± 0.05	2.37
k_{113}	0.29 ± 0.07	0.21
k_{114}	0.63 ± 0.04	0.72
k_{122}	-0.74 ± 0.03	-0.71
k_{124}	1.38 ± 0.02	1.41
k_{134}	1.71 ± 0.03	1.70
k_{144}	-0.03 ± 0.03	0.00
k_{315}	-0.79 ± 0.03	-0.90
k_{11}	-3.2 ± 0.9	-4.7
k_{13}	-8.6 ± 2.6	13.2
k_{14}	-2.4 ± 0.5	-2.2
k_{31}	-12.4 ± 3.0	3.4
k_{33}	-8.4 ± 6.8	-3.9
k_{41}	-4.4 ± 0.7	-4.1
q_{111}	$(-2.9 \pm 2.4) \cdot 10^{-21}$	$0.6 \cdot 10^{-21}$

Both parameter sets are calculated using the linear elastic constants according to [16] and the linear piezoelectric and dielectric constants according to [3]. Other relevant remarks are the same as for Table 1.

originating from various sources have been done before. As a rule the compared nonlinear constants were calculated using different sets of linear constants. This omission is rectified here. To achieve consistency with [1] the results of this work were recomputed using the elastic constants from McSkimmin, Andereatch, and Thurston [16] before they were entered into Table 3.

Given that a different set of elastic constants is used to make the comparison, the numerical coefficients in Table 2, depending on the linear material constants, have also changed. Their change is, however, very small, beyond the number of displayed decimal digits. As a result, no new version of Table 2 needs to be included in this paper. This entire comment is made only to assure the reader that such a possibility has been taken into account.

The effect of the linear constants on the nonlinear ones may be an interesting one but, at the same time, one that has been paid very little attention to. The comparison between the results of this work in Table 1 and 3 offer a qualitative preview of what can be expected.

6. Conclusion

This paper represents an attempt to determine simultaneously all four electromechanical nonlinearities existing in quartz: the third-order elasticity, the electroelasticity, the electrostriction and the third-order permittivity.

Fifteen parameters, for the main part linear combinations of the independent material constants describing these phenomena in quartz, have been determined using the least-square fit to one hundred and eighty-four experimental data provided by the resonator method.

The main reason for the number of determined parameters to be limited to 15 instead of the full number of 31 fundamental constants is a numerical one. The same numerical phenomenon provides a valuable insight into the function of the third-order elastic constants in the process of determination of the remaining nonlinearities (electroelasticity, electrostriction, third-order permittivity) by means of the resonator method. In particular, it shows that in order to determine these latter nonlinearities the use of third-order elastic constants from an external source cannot be avoided.

The work is a classical example of an independent verification process. The comparisons made with the nonlinearities determined separately by different authors and methods show an encouragingly high degree of agreement. At the same time, however, a few instances were noted with differences which may be statistically significant.

This study is based on a substantially larger number of observations (184) than is the total number of data (59) which have produced the values of the third-order electromechanical constants of quartz [1] external to this work. As such the present results carry some statistical weight. Any cases of disagreement between them and [1] are thus difficult to dismiss without an appropriate explanation which is yet to be found.

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