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PROBLEMS OF DETERMINATION OF THE COMPLETE SET OF THE NONLINEAR CONSTANTS OF QUARTZ[1]

Carl K. Hruska
Piezoelectricity Research Laboratory
Department of Mathematics and Statistics, York University
North York, Ontario M3J 1P3, Canada

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Nine independent phenomena are described that can degrade the quality of the calculated values of the third-order nonlinear material electromechanical constants of piezoelectric crystals. A significant role of one of them – the substitutions – has been identified in the process of determination of the current values of the nonlinear constants of α-quartz. This is sufficient to consider these values and their standard errors generally unreliable. To rectify the problem, the nonlinear constants should be recalculated using a simple new strategy which is described.

1. Introduction

The third-order nonlinear electromechanical constants of piezoelectric crystals include four tensors of material constants. They are the third-order elastic, elecroelastic, electrostrictive and third-order dielectric constants. The constants are defined in the natural state of the crystal by means of the cubic terms (hence the term 'third-order') of the thermodynamic potentials. In this work they are referred to briefly as the nonlinear constants.

Attempts to determine the nonlinear constants of piezoelectric crystals have been numerous and have stretched over a 30 years period. Most of the work has investigated α-quartz. With the search to replace quartz with new piezoelectric materials that have better properties, it is expected that the process of determining nonlinear constants will be repeated. Because of the much higher piezoelectric coupling of the new materials, there will be a keen interest in the process. In order to avoid repetition of earlier errors, this paper draws attention to the phenomena which may degrade the quality of the calculated nonlinear constants. They are described and illustrated using the lesson of quartz.

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The main body of knowledge about the electromechanical nonlinearities in α-quartz is represented by the four above tensors with their nonlinear constants referenced to zero strain and dc field. At this point there are two sets of values in use for each tensor. They have been determined in a complete (or a very near complete) form [1,2,3] using four independent data sets and three different experiments. It is believed that their values are unreliable and that they should be recalculated. This paper will show why and how.

2. Computation of nonlinear constants and sources of errors

The nonlinear constants of piezoelectric crystals are computed from experimental data using overdetermined linear systems such as

$$\mathbf{E} = \mathbf{M} \cdot \mathbf{X} + \mathbf{A}, \qquad (1)$$

where $\mathbf{E}$ is a column vector containing experimental quantities E_i, $i = 1, 2, \ldots, m$, $\mathbf{X}$ is a column vector of nonlinear constants commonly denoted x_j, $j = 1, 2, \ldots, n$, and $m > n$. $\mathbf{M}$ is a matrix of elements M_{ij} and $\mathbf{A}$ is a column vector of elements A_i; both $\mathbf{M}$ and $\mathbf{A}$ are functions of the linear (elastic, piezoelectric and dielectric) material constants of the investigated crystal, crystallographic orientation of the experimental specimens used, and the geometry and other characteristic features of the particular experiment which produces E_i. The definition of the functions is determined by the nonlinear theory linking the experimental data and the nonlinear constants. The numerical values of $\mathbf{M}$ and $\mathbf{A}$ are calculable and known when system (1) is formulated.

The values of the sought nonlinear constants x_j and their standard errors $\vartheta(x_j)$ are obtained from (1) using the least-squares fit [4]. A number of errors must be avoided or controlled in order to prevent a degradation of the results. Nine sources of these errors are described below and illustrated by examples from literature.

1.–3. Errors in the theory, linear constants and orientation angles

For the least-squares fit to produce valid results, the values in matrix $\mathbf{M}$ and column vector $\mathbf{A}$ must be free of errors. Ideally, this means that

(A) their analytical definitions obtained from the nonlinear theory should properly represent the link between the experimental data and the nonlinear constants;

(B) they should be calculated using correct linear constants of the crystal; and

(C) they should be calculated using exact orientations of the experimental specimens used.

Most of the effort to obtain realistic values of the nonlinear constants nas been centered on attempts to satisfy condition (A) with ever increasing accuracy. Classical examples are the improvements introduced in [6] over [5] and in [8] over [7]; in combination they resulted, for the first time, in attaining a good measure of agreement between the nonlinear constants of quartz obtained by two different experimental methods.

Severe violations of (A) have been quite common in the past; the possibility that some minor ones are still waiting to be spotted cannot be disregarded. However, all implementations of the nonlinear theory are likely to be only approximate. Therefore, the goal here is to reduce the errors due to theory to acceptable limits, i.e., safely below the level of unavoidable errors caused by experiments.

No perfect set of linear constants exists for any crystal and condition (B) is thus impossible to satisfy. To prevent serious distortions of the nonlinear constants, it is essential to use a set of a good quality. In the case of quartz, there exist a number of 'good' sets of linear constants and it is difficult argue which is the 'best' [9]. A study made by Hruska [10] shows that making a choice among the 'good' sets can appreciably affect the values of the nonlinear constants. In making a selection, the linear elastic constants are the most important to consider. Their values should have standard errors well below 1%.

Different authors use different sets of linear constants in their calculations. A consistent use of one set would be preferable, because it would remove an unnecessary source of inconsistency and thus enable the researcher to focus on those that are more serious.

It is not possible to expect that condition (C) be ever fully satisfied. However, a recent study made by Hruska [11] suggests that an orientation accuracy with the standard errors not exceeding several minutes is sufficient. In the past the accuracy of orientation has not always been reported and this is now seen as a drawback.

4. Systematic experimental errors

The only quantities in (1) that are allowed to include errors are the experimental quantities in $\mathbf{E}$, and these must be random experimental errors. Theoretically, they are the sole reason for the nonzero values of the standard errors $\vartheta(x_j)$.

The danger of systematic errors has been recognized in generating a well defined uniaxial stress [12] or a uniform transverse dc electric field [13] in quartz cubes. The same applies to the uniform lateral dc field in quartz plate resonators [14].

5. Under-representation

If, for some value of j, the magnitude of all products $M_{ij} \cdot x_j$ in system (1) is comparable with the random experimental errors if E_i, then the nonlinear constant x_j is under-represented in the system. Its value calculated from (1) will be associated with an excessively large standard error $\vartheta(x_j)$.

Large standard errors are known to plague the values of some electrostrictive constants. An example of their under-representation with all data readily available can be found in [8]. An attempt to remove the problem can be made by optimizing the design of the crystal samples used.

6. Small number of degrees of freedom

For the standard errors $\vartheta(x_j)$ to be reliable and interpretable in terms of the normal distribution, it is necessary that the difference $m - n$, known as the number of degrees of freedom, be made sufficiently large; 10 or less, as used in some studies, may not be adequate.

7. Arbitrary multipliers

All experimental values E_i in (1), viewed as random quantities, should have the same standard deviation. Failing that, each linear equation in (1) is to be adjusted by a suitably chosen multiplier. This is called 'weighting' and the 'ordinary' least-squares process is thereby replaced by the 'weighted least-squares' [4].

It appears that in some cases these multipliers are assigned to individual equations on the basis of an algebraic convenience rather than their true function. This alters the result of the least-squares proces. It may lead to an uncertainty as to what are the formally correct values of the nonlinear constants [15]. The uncertainty can reach tens of percent [16] and thus the use of arbitrary multipliers should be avoided.

8. Near colinearity

A phenomenon frequently present in matrix **M** is colinearity. It may be difficult to demonstrate analytically because the algebraic expressions of the matrix elements M_{ij} are rather complex. Only a single case of colinearity (predicted by numerical means in [17]) has been confirmed analytically by Kittinger and Tichy [18].

As pointed out by Hruska [19,20,21], the colinearity becomes a problem when turned into near colinearity. This happens when the matrix elements M_{ij} are not computed with sufficient accuracy. Then matrix $\mathbf{M}^T\cdot\mathbf{M}$, where $\mathbf{M}^T$ is the transpose of **M**, becomes ill-conditioned. Its inverse, crucial to the least-squares process, is then poorly computed. As a result, the least-squares algorithm will produce values of nonlinear constants which may be incorrect by several orders of magnitude as well as sign. Relevant examples can be found in [22,23].

To avoid the near colinearity, the matrix elements M_{ij} should be computed using the double or quadruple precision. Also, the values of the linear constants used in the calculations should fully reflect the crystal symmetry. A good example is provided by the elastic constants of quartz, where $c_{66} = 0.5(c_{11} - c_{12})$ due to symmetry. If, using the units of 10^9 N/m^2, $c_{11} = 86.74$ and $c_{12} = 6.99$, then $c_{66} = 39.875$ should be used and its rounded off value of 39.88 avoided.

9. Substitutions

According to past experience individual experiments are conducted in order to determine a selected subset ot the nonlinear constants (e.g., the third-order elastic constants) which is of interest at a given time. The choice of the experiment is made on the basis of providing an access – in principle – to the full number of the targeted constants. This is verified by forming and analyzing system (1), appropriate for the experiment, before the experiment is started.

As a rule, such an experiment does not provide access to the targeted nonlinear constants exclusively or without hindrance. There are always other, 'unwanted' nonlinear constants present in (1). Some of them form unresolvable linear combinations with the targeted ones (e.g., the third-order elastic combined with the electroelastic constants). To exploit the potential of the experiment and system (1) towards the determination of the targeted constants, the unwanted constants which have been determined earlier are substituted with their published values. In other cases, they are just disregarded, i.e., substitued with zeros, sometimes with a remark that their contribution is believed to be negligible.

The substitutions of published values or zeros are made prior to the least-squares fit which is then executed for the targeted nonlinear constants as the only unknown quantities remaining in the system. The results are then interpreted mechanically as the values and standard errors of there remaining constants.

A detailed study made by Hruska [24] shows that the above procedure leads to uncontrolled and unnoticed logical and numerical errors. Their character and seriousness depend on the algebraic and numerical properties of matrix **M** and on the quality of the substitued values. They always include one or more of the following: a numerical distortion and/or misinterpretation of the calculated values, a numerical distortion and/or misinterpretation of their standard errors, and a loss of valuable information.

The occurrence of the substitutions is very common; two real-life examples which also include an explanation of their consequences are in [24,25].

To prevent some of the undesired effects of the substitutions from happening and to appreciate the rest, the substitutions can be postponed until after the least-squares fit is executed [24]. They may then be found no longer desirable. If their impact is not fully understood, the substitutions should be avoided.

3. Current nonlinear constants of α-quartz

A complete set of the 14 third-order elastic constants of quartz was published for the first time by Thurston, McSkimin and Andreatch [1] in 1966. Used ever since, the constants were computed from observations [1,26] of changes in the transit time of acoustic pulses propagating through bulk quartz under the effect of a hydrostatic and unidirectional pressure. Although based on a rigorous application of nonlinear theory, the analysis of the experiment ignored all but the targeted third-order elastic constants. This means that the determined values and their standard errors suffer from the problems associated with 'Substitutions' as described above. As the order of magnitude of the disregarded nonlinear constants is now known, the damaging effect must be quite substantial numerically. For this reason it is difficult to accept these values as the correct material constants.

The remaining 17 nonlinear constants of quartz – 8 electroelastic, 8 electrostrictive and 1 third-order dielectric – were all obtained from data [8] on the dc field-induced changes in the transit time of the acoustic pulses. Observations of changes in the series resonance frequency of resonators subjected to a dc field bias [5,17,27,28] produced another set of these constants with three of them available only in unresolvable combinations.

The latest values of both sets have been computed by Hruska [2] in 1992. Unfortunately, in both cases, the desired constants had to be isolated from their combinations with the third-order elastic constants using their values from [1]. As a result, the current values of the electroelastic, electrostrictive and third-order dielectric constants, together with their standard errors, are not the desired material constants. The importance of this fact must not be played down by the huge success of the two methods which independently produced almost identical values of the electroelastic constants.

The work of Thurston et al. was repeated recently by Wang in the course of his Ph.D. work [3] of 1993. His aim was to determine the truly 'material' third-order elastic constants by including in the analysis of the experiment all participating nonlinear phenomena. Of necessity, the calculations had to involve values of the electroelastic, electrostrictive and third-order dielectric constants taken from an external source. As the only available values of these constants are unreliable, the new values of the third-order elastic constants themselves are likely to be afflicted by the same problem.

4. Conclusion

The nine potential sources of problems and errors encountered during the course of investigation of the nonlinear constants of α-quartz and described in this paper should be taken into account when the nonlinear or other material constants of piezoelectric crystals are sought in the future.

The problem associated with substitutions may not be the only reason but it is a sufficient one to conclude that the eight sets of the nonlinear constants of α-quartz discussed in this paper are not reliable and should be recalculated. This can be done by

(A) computing the nonlinear constants (and their combinations) obtainable from each available experimental data set separately and without making any substitutions;

(B) searching for and removing all statistically significant conflicts among the nonlinear constants obtained in (A). This may necessitate corrections of the theory of some of the experiments, a rejection of some experimental outliers, etc.; and

(C) combining all retained experimental data into one set and computing the nonlinear constants using a single least-squares process.

This should produce a complete set of 31 nonlinear constants of α-quartz, with each constant determined in isolation and free from the problems caused by substitutions.

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