ON THE EXACT CALCULATION OF ELASTIC CONSTANTS OF CRYSTALS FROM ULTRASONIC VELOCITIES ALONG ARBITRARY DIRECTIONS—APPLICATION TO SODIUM CHLORATE

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Abstract

A technique for evaluating the exact elastic constants of anisotropic crystals from ultrasonic velocities along arbitrary directions is developed. This involves a numerical iteration of the full cubic Christoffel equation to correct the approximate analytic expressions for the velocities in terms of the elastic constants. The method is tested on cubic sodium chlorate. From the three ultrasonic pulse echo velocities along an arbitrary direction the c_{ij} are evaluated. The results agree with the values obtained from simple [100] and [111] directions, *viz.*, $c_{11}=4.95$, $c_{12}=1.45$ and $c_{44}=1.14$ ($\times 10^{10}$ N/m^2).

1. Introduction

For any direction in a single crystal three types of waves, one quasi-longitudinal and two quasi-transverse, may be propagated. The three corresponding velocities are the roots of a cubic equation – the Christoffel equation – whose coefficients are functions of the elastic constants and the cosines of the direction of propagation of the sound. For highly asymmetric crystals, especially for general directions, the Christoffel equation

$$\left| \Gamma_{ik} - \delta_{ik}\, \rho\, v^2 \right| = 0\,, \quad i, k = 1, 2, 3 \qquad [1]$$

where $\Gamma_{ik} = c_{ijkl}\, \alpha_j\, \alpha_l$, α_j and α_l being the direction cosines, c_{ijkl} the stiffnesses, ρ the density of the material and v the wave velocity, cannot be resolved into pure modes. It is, therefore, customary to choose simple directions along which equation [1] may be solved easily.

However, in some crystal specimens this may not always be possible. Furthermore, in monoclinic and triclinic crystals one has few such simplifications by virtue of symmetry. Thus one has often to deal with the full cubic equation. Now in order to obtain all the constants at least as many velocities as the number of independent elastic constants are required. The calculation of elastic constants from ultrasonic velocity measurements along arbitrary

directions, even if in sufficient number, presents two main difficulties. Firstly, one has a set of simultaneous cubic equations. Secondly, the problem is opposite to the usual question of finding eigen values and eigen vectors, for here the eigen values are known, the eigen vectors are unknown and the coefficients of the matrix are the quantities to be found. Thus the determination of the elastic constants of a triclinic crystal, whose elastic behaviour is characterised by 21 independent constants and for which no reduction of equation [1] by virtue of symmetry is possible, is a task that has not been solved so far.

Hence it is undoubtedly necessary to develop a technique of solving the Cristoffel equation in its full cubic form. The present exact iteration technique was developed principally for application to monoclinic and triclinic crystals to be reported later. It was, however, necessary to check the method with respect to both accuracy and rapidity of convergence. This has been done by applying the technique to an arbitrary direction in a cubic crystal and is reported in this communication.

2. Development of Iteration Techniques for Solving Christoffel Equation

It is a common practice to take the direction of propagation as X_3' and $\rho v_i^2 = q_i$ as c_{33}', c_{44}' and c_{55}'. Sundara Rao[1-3], Bhimasenachar,[4,5] Mayer and Hiedemann[6] and others resorted to such an approach. But this is not quite correct. For propagation along X_3' direction one has,

$$\begin{bmatrix} c_{55}' - q & c_{45}' & c_{35}' \\ c_{45}' & c_{44}' - q & c_{34}' \\ c_{35}' & c_{34}' & c_{33}' - q \end{bmatrix} \begin{bmatrix} u_1' \\ u_2' \\ u_3' \end{bmatrix} = 0 \qquad [2]$$

The rotated constants c_{ij}' can be most conveniently read in terms of c_{ij} from available tables [7-9].

The zero order solution of the secular equation obtained by neglecting the off-diagonal terms, they being small, is :

$$q_1 = c_{55}', \quad q_2 = c_{44}' \text{ and } q_3 = c_{33}', \qquad [3]$$

where q_1 and q_2 are the quasi-transverse modes with displacements respectively along X_1' and X_2' and q_3 is the quasi-longitudinal mode. A computation of c_{ij} from the above linear equations will give only the zero order approximation to the values of the stiffnesses. This is the procedure adopted by the early workers

A better approximation would be to set

$$q_1 = c_{55}' + \epsilon_1, \quad q_2 = c_{44}' + \epsilon_2 \text{ and } q_3 = c_{33}' + \epsilon_3 \qquad [4]$$

The correction terms ϵ_i are usually small and neglecting ϵ_i^2 and ϵ_i^3 terms, their values obtained from equation [2] are :

$$\epsilon_1 = \frac{c'^2_{35}(c'_{44}-c'_{55}) + c'^2_{45}(c'_{33}-c'_{55}) - 2\,c'_{34}\,c'_{35}\,c'_{45}}{(c'_{44}-c'_{55})(c'_{55}-c'_{33}) + c'^2_{34} + c'^2_{35} + c'^2_{45}} \qquad [5a]$$

along with two similar expressions for ϵ_2 and ϵ_3 (Equations [5.*b*] & [5.*c*]). These ϵ_i are calculated using the zero order values of c_{ij} and the first order values of $c'_{55} = q_1 \quad \epsilon_1 \cdots$ will be obtained. Such an iteration procedure was adopted by Viswanathan and Raja Gopal[10] in the case of monoclinic sodium thiosulphate pentahydrate.

Neighbours and Smith[11] had earlier developed an approximation method to obtain c_{ij} from velocity measurements in the case of cubic crystals. They applied it to the case of nickel[12]. This is equivalent to neglecting the term $(c'^2_{34} + c'^2_{35} + c'^2_{45})$ in the denominator of equations [5]. Arenberg[13] adopted the method, namely neglecting the term $(c'^2_{34} + c'^2_{35} + c'^2_{45})$ in equation [5], to compute the c_{ij} of silver chloride. Armstrong and others[14] also followed in the same line. Later Neighbours[15] extended the method to hexagonal, tetragonal and orthorhombic classes. But the term $(c'^2_{34} + c'^2_{35} + c'^2_{45})$ contributes a fifth or more of the denominator in certain cases. Its neglect is not quite correct. More recently, Wachtman *et al*[16] have calculated the elastic constants of cubic $SrTiO_3$ from velocity measurements in a single arbitrary direction; their method which uses exact equation and an iteration procedure provides an alternative to Neighbours' method. It should also be pointed out that near highly symmetric directions, other procedures[17] are better suited and these have been used by Krishnan *et al*[18].

3. Outline of the Present Method

The iteration technique based on equation [5] is basically incomplete because their values of ϵ_i are only the approximate solutions of the cubic equations for the residues $\epsilon_1 = q_1 - c'_{55}$, $\epsilon_2 = q_2 - c'_{44}$ and $\epsilon_2 = q_2 - c'_{33}$. Therefore a solution of equations [4] and [5], while a better approximation than equation [3] is not equivalent to full solutions of the Christoffel equation.

A numerical procedure of successive approximations which yields the exact corrections ϵ_1, ϵ_2 and ϵ_3 may be devised as follows. Suppose the zero order values of c_{ij} are obtained and ϵ_i introduced through equation [4]. The exact equations to be satisfied by ϵ_i are :

$$\epsilon_1^3 + \epsilon_1^2(2c'_{55} - c'_{33} - c'_{44}) + \epsilon_1[(c'_{33}-c'_{55})(c'_{44}-c'_{55}) - c'^2_{34} - c'^2_{35} - c'^2_{45}] + [c'^2_{45}(c'_{33}-c'_{55}) + c'^2_{35}(c'_{44}-c'_{55}) - 2\,c'_{34}\,c'_{35}\,c'_{45}] = 0 \qquad [6.a]$$

$$\epsilon_2^3 + \epsilon_2^2 (2c'_{44} - c'_{55} - c'_{33}) + \epsilon_2 [(c'_{55} - c'_{44})(c'_{33} - c'_{44}) - c'^2_{34} - c'^2_{35} - c'^2_{45}] + [c'^2_{34}(c'_{55} - c'_{44}) + c'^2_{45}(c'_{33} - c'_{44}) - 2c'_{34}\, c'_{35}\, c'_{45}] = 0 \qquad [6.b]$$

$$\epsilon_3^3 + \epsilon_3^2 (2c'_{33} - c'_{44} - c'_{55}) + \epsilon_3 [(c'_{44} - c'_{33})(c'_{55} - c'_{33}) - c'^2_{34} - c'^2_{35} - c'^2_{45}] + [c'^2_{34}(c'_{44} - c'_{33}) + c'^2_{35}(c'_{55} - c'_{33}) - 2c'_{34}\, c'_{35}\, c'_{45}] = 0 \qquad [6.c]$$

If one could obtain the analytical expressions for the roots of equations [6] and if one could further solve the simultaneous equations [4] one would get the exact values of the elastic constants c_{ij}. It is not possible to effect this and therefore recourse must be had to numerical methods. The deficiency of the earlier iteration methods based on equations [5] is the linearization of equations [6] to get the roots. Now with the availability of convenient Tables[12] for the numerical roots of cubic equations, there is no difficulty in solving equations [6] for the roots ϵ_i of the cubic equation.

Therefore the numerical procedure for getting the exact values of c_{ij} would be as follows. Use the zero order values of c_{ij} as obtained from equation [3] in equations [6] and solve for the ϵ_i of the cubic equations. These are the exact zero order corrections $\epsilon_1 = q_1 - c'_{55}$, $\epsilon_2 = q_2 - c'_{44}$ and $\epsilon_3 = q_3 - c'_{33}$. The corrected set $c'_{55} = q_1 - \epsilon_1$, $c'_{44} = q_2 - \epsilon_2$ and $c'_{33} = q_3 - \epsilon_3$ is the first order approximations to c'_{55}, c'_{44} and c'_{33} which are then solved to get the first order values of c_{ij}. The first order values of the corrections ϵ_i may then be found out and the iteration procedure is continued until the convergent limit is approached to the desired accuracy. The convergent limit satisfies equations [4] and [6] simultaneously and hence equation [2] also. These are therefore the 'true' elastic constants of the crystal.

The Christoffel equation [1] involves only squares of the various direction cosines while equation [2] involves fourth powers of the direction cosines. All the same, the roots of the two equations are identical, because the matrices Γ and c' are related by an orthogonal transformation and it is well known that the eigen-values of a matrix are invariant under an orthogonal transformation. The equivalence of the solutions of equations [1] and [2] has been explicity checked by proving the term-to-term correspondence of the coefficients.

It should also be added that the iteration procedure is best done with equation [2] rather than with equation [1]. Firstly, Γ_{11}, Γ_{22} and Γ_{33} do not contain all the c_{ij}'s and it is impossible to evaluate all the constants in crystals of low symmetry. Secondly, the association of c'_{44} and c'_{55} with the vibration directions is straightforward in equation [2], while this correspondence is not easy in the original Christoffel equation. Thirdly, the off-diagonal terms in Γ_{ij} are comparatively larger than those in c'_{ij}. The lowest diagonal term in Γ_{ij} matrix is $\Gamma_{11} = 1.436$ while the largest off-diagonal term $\Gamma_{23} = -0.866$ in units of $10^{10}\ N/m^2$. In the c'_{ij} matrix the situation $c'_{55} = 1.291$ and $c'_{34} = 0.284$ favours a rapid convergence of the iteration procedure.

4. APPLICATION TO $NaClO_3$

To test the validity of the new procedure as well as to get an indication of the speed of convergence such a calculation was applied to the cubic sodium chlorate $NaClO_3$. The crystal has been investigated by many earlier workers[20–27]. Sodium chlorate was chosen because large flawless crystals can be obtained for a comparative investigation and also to supplement our measurement on the isomorphous sodium bromate[28].

Single crystals of $NaClO_3$ (BDH Laboratory reagent quality), oriented along the [100] and [111] directions were grown by slow evaporation of the aqueous solution. From a block of size approximately $40 \times 31 \times 14$ mm. oriented along the [100] axis, a smaller piece was ground to a thickness of 6·82 mm. in order to obtain a pair of smooth, flat and parallel faces, inclined to all the three mutually perpendicular crystallographic directions. The inclinations to the crystal axes were measured by means of an optical goniometer correct to 1 minute of arc. The specimen used is schematically shown in Figure 1.

The velocities of the quasi-longitudinal and the two non-degenerate quasi-transverse waves were determined by the ultrasonic pulse echo method using unrectified pulses at 10 MHz. Details of the set up are found elsewhere[29]. In order to obtain the transverse wave velocities, first the Y-cut

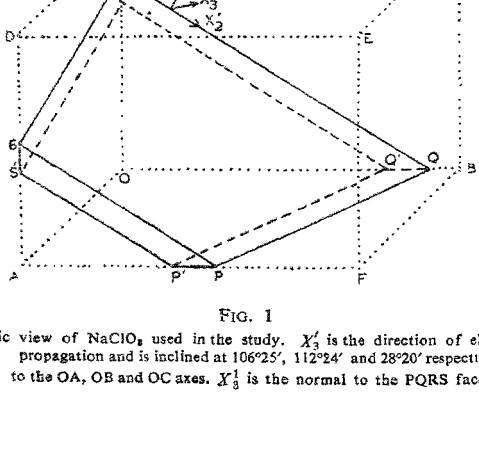

FIG. 1

Schematic view of $NaClO_3$ used in the study. X_3' is the direction of elastic wave propagation and is inclined at 106°25′, 112°24′ and 28°20′ respectively to the OA, OB and OC axes. X_3^1 is the normal to the PQRS face.

transducer was oriented with vibration direction along the longer edge of the specimen (perpendicular to X_1 axis, see Figure 1). The transducer was then rotated through 90° about this direction and the velocity measured for the second time. With this information it was possible to complete the direction cosine scheme of all X_1', X_2' and X_3' axes with respect to X_1, X_2 and X_3 and the result is shown in Table I.

TABLE I

Direction cosines for the Orientation of the plate

	X_1	X_2	X_3
X_1'	0.959_2	-0.112_3	0.259_3
X_2'	0.0	0.917_7	0.397_3
X_3'	-0.282_6	-0.381_1	0.880_2

The velocity measurements were made at 25°C. Taking the density to be 248_5 kg/m^3, the values of q_i obtained were $q_1 = 1.25_2$, $q_2 = 144_0$ and $q_3 = 4.55_2$, in 10^{10} N/m^2.

The rotated constants c_{ij}' were then expressed in terms of c_{ij} and the known direction cosines using the well known expressions[7-9]. The values are given in Table II. The zero order values of c_{ij} obtained with equation [3] were $c_{11} = 5.^{1}48$, $c_{12} = 1.452$ and $c_{44} = 1.048$ in units of 10^{10} N/m^2. The exact zero order corrections ϵ_i obtained using these values were $\epsilon_1 = -0.0491$, $\epsilon_2 = -0.0119$ and $\epsilon_3 = 0.0611$. The first order values of elastic constants were $c_{11} = 4\,970$, $c_{12} = 1\,411$ and $c_{44} = 1.137$ ($\times 10^{10}$ N/m^2). The subsequent values of ϵ_i were $-0\,0387$, $-0\,0017$ and $0\,0405$ respectively, the values obtained from the final approximation being -0.0386, $-0\,0012$ and $0\,0399$ for ϵ_1, ϵ_2 and ϵ_3 respectively by which time the computational precision exceeded the experimental accuracy of measurement of elastic constants, *viz.*, $\pm 0.5\%$ for c_{11} and c_{44} and $\pm 1\%$ for c_{12}. The convergence of the elastic constants calculated is shown in figure 2, the limiting values being $c_{11} = 4.99_0$, $c_{12} = 1.45_3$ and $c_{44} = 1.12_7$, all in $10^{10} N/m^2$ units.

TABLE II

Values of the rotated elastic constants

c_{ij}' in terms of c_{ij}.

$$c_{33}' = 0.6278\ c_{11} + 0.3720\ c_{12} + 0.7440\ c_{44}$$
$$c_{44}' = 0.2246\ c_{11} - 0.2224\ c_{12} + 0.5109\ c_{44}$$
$$c_{55}' = 0.1274\ c_{11} - 0.1274\ c_{12} + 0.7451\ c_{44}$$
$$c_{34}' = 0.2203\ c_{11} - 0.2201\ c_{12} + 0.4402\ c_{44}$$
$$c_{35}' = 0.1614\ c_{11} - 0.1614\ c_{12} + 0.3228\ c_{44}$$
$$c_{45}' = 0.0648\ c_{11} - 0.0648\ c_{12} + 0.1296\ c_{44}$$

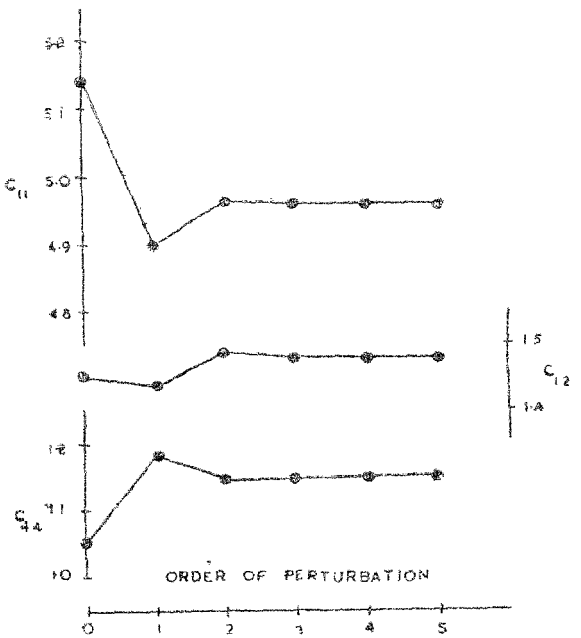

FIG. 2
Convergence of the elastic constants

5. DISCUSSION

The present procedure is seen to be sufficiently convergent so as to be practicable in more complicated crystals. The point regarding the absolute accuracy of the method needed to be settled. This was done in two ways.

Firstly, velocity along [100] and [111] directions were measured using crystals grown from the same batch of material; c_{11} and c_{44} were obtained from the longitudinal and shear velocities along [100] and c_{12} was derived as the mean of the two measurements along [111] (both of which yielded results to within 0.02%). The values were $c_{11} = 4.94_7$, $c_{12} = 1.45_3$ and $c_{44} = 1.13_6$ in units of 10^{10} N/m^2.

On comparing with the values deduced from the measurements along arbitrary directions c_{11} is larger by 1% and c_{44} is less by about 1%. Now the errors in the direct evaluation of c_{ij} from [100] and [111] directions are of the order 0.5% for c_{11} and c_{44} and 1% for c_{12}. The accuracy of the velocity measurements along arbitrary directions is slightly inferior because of the degeneration of the echo pattern caused by the difference in the directions of propagation of the ultrasonic pulse and the ultrasonic energy. In view of this, the difference between the sets of c_{ij} must be considered within the overall accuracy of the measurements. In other words, the measurements along arbitrary directions yield the "true" elastic constants when the present iteration procedure is applied.

A second way of checking the accuracy of the procedure was to substitute the values of c_{11}, c_{12} and c_{44} in the Christoffel equation [1] and to see if the equation was identically satisfied. The actual residues with the derived values of c_{ij} were - 0.0009, 0.0000 and - 0.0005 which are entirely negligible.

Finally, the present iteration procedure has two special features which are of great advantage in the process of numerical computation. Firstly, since we are solving the full Christoffel equation we must get three real velocities. Thus the roots of equation [6 *a*] when combined with c'_{55} yield the same three velocities as the sum of c'_{44} and the three roots of equation [6.*b*] and the three sums of c'_{33} with the three roots of equation [6 *c*]. To give an example in the first order correction process the three roots are: $\epsilon_1 = 0.1761$, -0.0491 and 3.3611; $\epsilon_2 = -0.0119$, -0.2371 and 3.1731 and $\epsilon_3 = -3.1239$, -3.3491 and 0.0611. Their combination with the zero order values $c'_{55} = 1.252_0$, $c'_{44} = 1.440_0$ and $c'_{33} = 4.552_0$ yield only three distinct velocities, 1.428_1, 1.202_9 and 4.613_1 thereby affording a constant check on the numerical calculations. Secondly, the trace of the determinant (2) is invariant and so the sum $(c'_{55} + c'_{44} + c'_{33})$ must be a constant in any step of approximation. In effect, this means that with the correct choice of ϵ_1, ϵ_2 and ϵ_3 the sum $(\epsilon_1 + \epsilon_2 + \epsilon_3)$ must be zero: The vanishing of the sum can be checked from the numerical values given earlier for ϵ_i in the various orders of approximations. In linearizing the cubic equations [5] to get the approximate values of ϵ_i, these two advantages are lost.

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