ELASTIC CONSTANTS OF PIEZO-ELECTRIC CRYSTALS

Zinc Sulphide

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1. *Introduction*

ATANASOFF and HART[1] evolved a method of determining the elastic constants of piezo-electric crystals. These authors directly measured the frequencies of piezo-electric vibration of plates of known orientation cut from the mother crystal. Since such frequencies are related to the elastic constants, the latter are easily evaluated if data regarding a sufficient number of plates is available. The plates were made to vibrate piezo-electrically as a filter between a variable frequency, stable oscillator and a vacuum tube volt-meter for detecting resonance frequencies of the plates. The case of quartz has been dealt with by them in this manner.

Diffraction of light by ultrasonic waves set up in liquids observed first in 1932 by Lucas and Biquard[2] and by Debye and Sears[3] provides us with a new and delicate method of detecting the resonance frequencies of a piezo-electrically vibrating crystal plate. X-cut quartz plates are now frequently used for setting up ultrasonic waves in liquids and a considerable literature has grown around this subject. The present authors have, however, found that a suitably cut crystal plate of any piezo-electric material such as zinc blende or tourmaline can be just as successfully employed in such investigations. In all such cases, the appearance of diffraction fringes in the usual arrangement can be taken as a delicate test for detecting the resonance frequencies of the plate under investigation. If the resonance frequencies of a sufficient number of differently oriented plates in a given crystal are thus detected and measured, the elastic constants may be calculated.

The above statements apply generally to all classes of piezo-electric crystals but in this paper, only the cubic system is dealt with and zinc sulphide belonging to the tetrahedral group of the cubic system (T_D class) is investigated in detail. This is a typical example of piezo-electric substances crystallising in the cubic system.

2. *Propagation of Sound Waves Along a General Direction in a Cubic Crystal*

In general, a sound wave travelling along a particular direction within a crystal can have three different velocities. The mathematical relationships existing between the elastic constants and the velocities of propagation of waves along different directions in such cases have been known for many years.[4] The theory, however, is applicable only to infinite plates and we shall first state the important results. The following determinantal equation gives three real positive roots for v^2 for a given set of values l, m, n and these three roots represent the squares of the three possible velocities for a sound wave travelling in the direction l, m, n in the crystal.

$$\begin{vmatrix} \lambda_{11} - \rho v^2 & \lambda_{12} & \lambda_{31} \\ \lambda_{12} & \lambda_{22} - \rho v^2 & \lambda_{23} \\ \lambda_{31} & \lambda_{23} & \lambda_{33} - \rho v^2 \end{vmatrix} = 0$$

l,m,n are the direction cosines of the axis along which the sound wave is travelling and λ's are given by the following equations:—

$$\lambda_{11} = C_{11}l^2 + C_{66}m^2 + C_{55}n^2 + 2C_{56}mn + 2C_{15}nl + 2\,C_{16}lm$$

$$\lambda_{12} = C_{16}l^2 + C_{26}m^2 + C_{45}n^2 + (C_{46} + C_{25})\,mn + (C_{14} + C_{56})\,nl + (C_{12} + C_{66})lm$$

$$\lambda_{31} = C_{15}l^2 + C_{46}m^2 + C_{35}n^2 + (C_{45} + C_{36})\,mn + (C_{13} + C_{55})\,nl + (C_{14} + C_{56})\,lm$$

$$\lambda_{22} = C_{66}l^2 + C_{22}m^2 + C_{44}n^2 + 2C_{24}mn + 2C_{46}nl + 2C_{26}\,lm$$

$$\lambda_{22} = C_{56}l^2 + C_{24}m^2 + C_{34}n^2 + (C_{44} + C_{23})mn + (C_{45} + C_{36})nl + (C_{46} + C_{25})lm$$

$$\lambda_{33} = C_{55}l^2 + C_{44}m^2 + C_{33}n^2 + 2C_{34}mn + 2C_{35}nl + 2C_{45}lm$$

The C's in these equations are the elastic constants. In the case of a cubic crystal, there are only three independent constants given by $C_{11} = C_{22} = C_{33}$ and $C_{12} = C_{13} = C_{23}$ and $C_{44} = C_{55} = C_{66}$, all others vanishing. The determinant then takes the following simple form:

$$\begin{vmatrix} C_{11}l^2 + C_{44}(m^2 + n^2) - \rho v^2 & (C_{12} + C_{44})lm & (C_{12} + C_{44})ln \\ (C_{12} + C_{44})ml & C_{11}m^2 + C_{44}(l^2 + n^2) - \rho v^2 & (C_{12} + C_{44})mn \\ (C_{12} + C_{44})nl & (C_{12} + C_{44})nm & C_{11}n^2 + C_{44}(l^2 + m^2) - \rho v^2 \end{vmatrix} = 0$$

The determinant may be further simplified if specific directions are considered. The roots obtained in three special cases in all of which the determinant splits into three linear equations, are given below. ρ is the density of the medium.

Propagation of the wave along	l, m, n	$v_1^2 \rho$	$v_2^2 \rho$	$v_3^2 \rho$
[001] axis	0, 0, 1	C_{11}	C_{44}	C_{44}
[111] axis	$\frac{1}{\sqrt{3}}, \frac{1}{\sqrt{3}}, \frac{1}{\sqrt{3}}$	$\frac{C_{11}+2C_{12}+4C_{44}}{3}$	$\frac{C_{11}-C_{12}+C_{44}}{3}$	$\frac{C_{11}-C_{12}+C_{44}}{3}$
[011] axis	$0, \frac{1}{\sqrt{2}}, \frac{1}{\sqrt{2}}$	$\frac{C_{11}+C_{12}+2C_{44}}{2}$	C_{44}	$\frac{C_{11}-C_{12}}{2}$

The root occurring under $v_1^2 \rho$ in each case represents the longitudinal vibration and those under $v_2^2 \rho$ and $v_3^2 \rho$ represent the transverse vibrations. In the case of cubic crystals, it is easy to cut plates which are parallel to various crystallographic faces and it has been found that in such cases, the manner of excitation and detection adopted in this investigation enables us to deal with only the thickness longitudinal vibrations. From the measured velocities of such vibrations, the effective elastic constants appropriate to the plates chosen can be calculated. In the case of a cubic crystal, there appear, however, certain special difficulties as two of the three plates enumerated above are not piezo-electrically excitable. Thus independent measurements have also to be made by employing static and other methods before values of reasonable accuracy can be arrived at.

3. *Experimental Arrangements*

A crystal of zinc sulphide* showing clearly defined and well developed faces is chosen and a number of sections parallel respectively to the 001, 111, 011 and 221 planes are cut and ground to uniform thickness. Care is taken to see that the specimen chosen does not exhibit twinning. The plates used in the present investigation are a few centimeters in length and breadth and less than two millimeters in thickness. Errors due to finite size are thus minimised. The faces in each case are silvered in the usual manner and the plate is made to oscillate by applying an alternating electric field obtained from a Hartley Oscillator circuit. The crystal holder is so made that one of the faces of the crystal can be brought into contact with the surface of a liquid like carbon tetrachloride or water contained in a cubical vessel as in experiments designed to study the diffraction of light by stationary ultrasonic waves in liquids. As the variable capacity in the oscillatory circuit is continuously altered, positions where the diffraction patterns are clearly

* Chemical analysis of the sample used gives the following results: Moisture 0·075%; SiO_2 2·155%; $Fe_2O_3+Al_2O_3$ 3·74%; Cu 1·03%; ZnS 93·64%. We are indebted to Mr. D. Venkateswarlu for this analysis.

seen may easily be picked out and identified as positions at which the crystal plate is oscillating in resonance with the oscillator and communicating its oscillations to the liquid. The frequencies at all such positions are measured with a standard heterodyne wave-meter and the corresponding velocities obtained by multiplying the frequency with twice the thickness of the plate or fractions thereof according as the crystal plate is oscillating in its fundamental or in one of its harmonics. The thickness and density of the plate under investigation are measured separately. With a given plate, a number of frequency readings are usually taken and the average obtained for deriving the elastic constants.

4. *Piezo-Electric Properties of Zinc Sulphide*

There is only one piezo-electric constant in the case of cubic crystals and this may be designated as e_{14} in Voigt's notation.[5] The components of strain will be related to the components of piezo-electric moment in accordance with the relationships

$$P_x = e_{14} \cdot yz; \qquad P_y = e_{14} \cdot xz; \qquad P_z = e_{14} \cdot xy.$$

It may now be shown that in the case of the 001 and the 110 plates, an electric moment applied along the axis normal to the plates will only cause strong tangential strains which by their very nature are incapable of being communicated to the liquid. In agreement with this expectation, we are unable to obtain any diffraction patterns for these two sections. An electric moment so applied in the case of the 111 and 221 plates will cause strong longitudinal strains. In the case of the 111 plates, the longitudinal effect is indeed found to be very strong as is to be expected from the theory. The result obtained from the 221 plate in this manner also refers to the longitudinal effect but may not be used to give independent results as it differs only by a small amount from that of the 111 section on account of certain special conditions that exist in this crystal. It has accordingly been employed for furnishing an additional check.

In deriving the constants themselves, the value obtained for $v_1^2 \rho$ in respect of the 111 plate is combined with two other observations. A special transmission method, designed in this laboratory and described in the previous paper[6] enables us to obtain C_{11} from a 001 plate. The usual static torsion method† enables us to obtain C_{44} by working on a plate, the length of which is parallel to a cube edge. The third constant C_{12} is obtained by elimination. As has already been mentioned, the effective elastic constants

† This method is based on principles of static torsion applicable to plates. Details are given in the foregoing paper.

obtained by employing the piezo-electric method of this paper in respect of the 221 section and the transmission method in respect of the 110 section are used as additional checks.

5. *Results*

The following table gives the results:

TABLE I

Elastic Constants of Zinc Sulphide

Plate	Thickness cm.	Density gm. per c.c.	Observed fundamental Mc. per sec.	Identification of the mode	Method employed	Elastic constant dynes per sq. cm.
001	0·102	4·109	2·512	Thickness Longitudinal	Transmission	$C_{11} = 10{\cdot}79 \times 10^{11}$
111	0·197	4·078	1·481	,,	Piezo-electric	$\frac{C_{11}+2C_{12}+4C_{44}}{3} = 13{\cdot}90 \times 10^{11}$
110	0·102	4·061	2·790	,,	Transmission	$\frac{C_{11}+C_{12}+2C_{44}}{2} = 13{\cdot}15 \times 10^{11}$
221*	0·1936	4·078	1·493	,,	Piezo-electric	$\frac{11C_{11}+16C_{12}+32C_{44}}{27} = 13{\cdot}64 \times 10^{11}$

* In this case, the cubic does not split into linear equations. The effective elastic constant given corresponds approximately to the observed longitudinal velocity.

Combining the first two results with the result $C_{44} = 4{\cdot}12 \times 10^{11}$ determined in this laboratory by the static torsion method, we obtain

$$C_{11} = 10{\cdot}79 \times 10^{11}; \quad C_{12} = 7{\cdot}22 \times 10^{11}; \quad C_{44} = 4{\cdot}12 \times 10^{11}.$$

If these values are substituted for the constants in respect of 110 section, we obtain $13{\cdot}13 \times 10^{11}$ which checks very well with the observed result. If they are substituted for the constants in respect of 221 section, we obtain $13{\cdot}56 \times 10^{11}$ which checks well with the observed result.

6. *Discussion of Results*

The elastic constants given in this paper lead to a bulk modulus of zinc blende $K = (C_{11} + 2C_{12})/3 = 8{\cdot}41 \times 10^{11}$ dynes per sq. cm. which may be compared with the figure of $7{\cdot}66 \times 10^{11}$ available in the literature.[7] Voigt[8] determined the elastic constants of zinc blende by static methods and obtained the following values:

$$C_{11} = 9{\cdot}43 \times 10^{11}; \quad C_{12} = 5{\cdot}68 \times 10^{11}; \quad C_{44} = 4{\cdot}37 \times 10^{11}.$$

There is agreement in the order of magnitude between these results and those obtained by us. The approximate equality of C_{11} and $C_{12}+C_{44}$ may be noted[9].

7. *Summary*

An experimental method of detecting and measuring the resonance frequencies of piezo-electric crystal plates is described. The elastic constants of zinc blende have been obtained by this method as $C_{11} = 10 \cdot 79 \times 10^{11}$; $C_{12} = 7 \cdot 22 \times 10^{11}$ and $C_{44} = 4 \cdot 12 \times 10^{11}$ dynes per sq. cm.

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