A SIMPLEx Technique FOR THE STUDY OF THE
ELASTICITY OF CRYSTALS*

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Abstract

A brief review is given of the use of the composite piezoelectric oscillator for determination of the elastic constants of small samples. A few preliminary results for single crystals have been obtained, for comparison with older measurements.

Introduction

Of some hundreds of important crystals, the elastic constants are known for about forty, including artificially-grown metals and alkali halides (Birch, et al., 1942, pp. 66–70). Many of the measurements on natural crystals of low symmetry were made by Voigt in an arduous study of the static bending and twisting of crystalline bars or plates. Voigt probably accomplished nearly all that is possible with natural crystals by these methods, for which fairly large samples are required. Recent advances have been possible partly because of the production of relatively large synthetic crystals, partly because of the development of new methods which permit the use of smaller samples. It is the purpose of this note to draw attention to the existence of a method applicable to many minerals which rarely occur in large sizes. Mineralogists, who have first access to mineral specimens and are familiar with problems of crystal orientation and crystal symmetry, may be encouraged by the simplicity of the experimental arrangements to undertake further studies in this relatively neglected field.

In recent years, a number of dynamic methods of measuring elasticity have come into use; the one to be described is the method of the composite piezoelectric oscillator which has been employed in a number of important investigations by Quimby (1925), Balamuth (1934) and others (Cady 1946, p. 484). In this technique, a small sample in the form of a prism of uniform cross-section, is cemented to a piezoelectric crystal, usually quartz, whose natural resonant frequencies are known. Under suitable restrictions, determination of the resonant frequency of the composite oscillator then leads to a value for the resonant frequency of the sample alone, from which, together with the dimensions and the density, one elastic constant or one combination of elastic constants, may be computed.

There is no way of avoiding the inherent complexity of crystal elas-

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ticity; in order to determine all of the elastic constants, there must be at least as many measurements, for rods of different orientations and for vibrations in different modes, as there are independent elastic constants. The other remaining difficulties are those of cutting and orienting the sample bars. In preliminary studies, samples as short as about 7 mm. have been used, but there seems to be no reason to take this as a lower limit. Samples several millimeters long should be obtainable from a considerable number of hitherto unstudied crystalline varieties.

**Theory**

A theory of two- and three-part composite oscillators may be found in the papers by Balamuth (1934) and Rose (1936). Consider two rods of the same, uniform, cross-section, and let rod 1 be the sample, rod 2 the piezoelectric crystal. Let the masses of the two rods be \( m_1 \) and \( m_2 \), respectively, their individual frequencies, \( f_1 \) and \( f_2 \). The frequency \( f \) of the composite oscillator formed by cementing these rods end to end is given by (Rose, 1936):

\[
(1) \quad m_1 f_1 \tan \frac{\pi f}{f_1} + m_2 f_2 \tan \frac{\pi f}{f_2} = 0.
\]

Thus if \( f \) and \( f_2 \) can be determined experimentally, \( f_1 \) may be found by (1). This relation is much simplified if \( f, f_1 \) and \( f_2 \) are all nearly equal. If \( f_1 \) and \( f_2 \) are within about 10% of \( f \), then the following equation is valid to within a per cent or so:

\[
(2) \quad f_1 = f + (f - f_2) m_2/m_1.
\]

This convenient approximation to (1) is often sufficiently exact.

The piezoelectric crystal may be cut so that it will be excited in extensional vibrations or in torsional vibrations. For extensional vibrations of thin bars, the lowest frequency of the sample alone, \( f_1 \), is related to its length \( l \) and density \( \rho \) by the relation, \( 2 f_1 l = \sqrt{E/\rho} \), where \( E \) is the "Young's modulus" in the direction of the axis of the rod. For bars having a length less than three or four times the diameter, a correction is required, which has been worked out for isotropic materials by Bancroft (1941). Assuming that this theory is approximately valid for crystals, we may conclude that the correction is less than 1% so long as the length is greater than twice the diameter, and "Poisson's ratio" is less than 0.3. There is no correction of this kind for torsional vibrations of rods of circular cross-section, for which the lowest frequency is related to the modulus of rigidity or torsion \( G \) about the axis of the rod according to \( 2 f_1 l = \sqrt{G/\rho} \). Equations (1) or (2) will hold approximately even if the cross-sections of sample and piezoelectric crystals are not exactly equal, except that for torsional vibrations the moments of inertia of the sections
about the axis should be substituted for the masses. The shape of the cross-section is not of consequence for thin bars in extensional vibration, but the theory of torsional vibration becomes more complicated for sections of other than circular shape (Cady, p. 113). Consequently the most useful shape for samples is the circular cylinder, preferably having its length several times its diameter.

Equations (1) and (2) are not restricted to the lowest or fundamental modes, and it is often more convenient to excite the driving crystal in an overtone than to employ a smaller crystal for which the same frequency would be the fundamental; on the other hand a large ratio of masses, \(m_2/m_1\), exaggerates the effect of the frequency difference \(f - f_2\).

The relations between \(E\) and \(G\), the orientation and the individual elastic constants of the sample are given by Voigt, Cady, and for certain cases, by Wooster.

**Experimental Arrangements**

The detection of the resonant vibration of a piezoelectric crystal depends upon the fact that at resonance, the impedance of the crystal undergoes a marked reduction which may be recognized by a variety of methods. The resonance curves for quartz and for most single crystals are extremely narrow, so that the first requirement is a source of variable frequency with fine frequency control through the correct range. The oscillator should supply a voltage of the order of 10 or more volts across the crystal and the series resistor \(R\), of perhaps 0.5 megohm (Fig. 1).

![Fig. 1. Schematic circuit for detection of resonance of the composite oscillator.](image-url)
A vacuum-tube voltmeter, with a short-period meter, or a cathode-ray oscilloscope, is connected across $R$. As the frequency of the voltage is varied, resonance is indicated by a sharp swing of the meter or a rapid modulation of the pattern on the oscilloscope screen. The voltage across $R$, small for frequencies away from resonance, may rise as much as several volts at resonance.

There are various methods of calibrating the frequency scale, which depend upon the available equipment. A number of standard frequencies are broadcast from the Bureau of Standards. Crystals which resonate at accurately-determined frequencies may be obtained from a number of manufacturers. Unless the dimensions are unusually well-determined, it is not worth while to measure the frequency more accurately than to about $1/1000$; other uncertainties are likely to approach $1\%$. In the present work, the 1000-cycle standard frequency signal of the Cruft Laboratory is used as the reference frequency, and applied to the horizontal axis of an oscilloscope. The signal from the variable frequency source is applied to the vertical axis. Observation of the Lissajous figures produced by this arrangement gives a great number of fixed points on the frequency scale, at 1000-, 500-, or even 100-cycle intervals. A precision capacitor is used for interpolation between these fixed frequencies.

For the minimum disturbance of the resonant frequency, the oscillator should be supported at displacement modes. In the fundamental extensional mode, the plane normal to the axis through the center of the rod is a node for longitudinal displacement, but the lateral displacement is a maximum in this plane. The lateral motion is small for quartz, however, and support by a spring clip at this position has a negligibly small effect on the frequency. It is not even essential to place the clip at the exact center, though the amplitude of resonance is reduced if the departure from the central position is marked. The two leaves of the clip are separately fastened to an insulating strip, and are used as the electrical connections to the quartz oscillator.

For extensional vibrations, X-cut quartz bars of square cross-section are convenient. The faces normal to the electric axis are coated with a thin conducting film: sputtered gold surfaces are most durable, but serviceable electrodes may be made either by pasting on thin metal foil or by painting with a conducting paint such as silver paste or even Aquadag. Rose (1936) has described a quartz oscillator of circular cross section which may be excited in torsional modes. This oscillator has four electrodes, connected in pairs, for which foil is well adapted. The crystal may be supported by clips at its central plane without disturbance of the frequency.

The composite oscillator is formed by cementing the sample of
unknown frequency to a quartz oscillator. A number of cements will
serve, such as DeKhotinsky wax or shellac flakes, and probably many
others. The shellac is softened on an electric plate, and applied sparingly
to the two ends to be joined, which are also warmed. The two rods are
then pressed together and allowed to cool. A strong joint is not required,
since, if the frequencies are properly matched, the interface is a plane of
zero stress, but there should be a minimum of space between the rods,
and a minimum of foreign material. Soft waxes or cements having high
internal friction are undesirable. The composite oscillator is placed in
the spring clip with the quartz oscillator centered on the clip (for the
fundamental modes), just as for the quartz alone.

RESULTS

No systematic investigation has as yet been completed, but the method
has been tested upon a set of samples of single crystals originally selected
by Professor Charles Palache for use in investigations of compressibility
by Professor P. W. Bridgman, in whose papers (1925, 1928, 1949) brief
descriptions may be found. These samples ranged in length from about
1 inch down to 0.5 inch; some were ground to a uniform cross-section,
others were bounded by natural prism faces. A few were too irregular
for the present purpose. In no case were there enough samples for the
determination of all of the elastic constants, but comparison with meas-
urements by other observers is possible in a number of instances.

A set of X-cut quartz oscillators of square cross-section was prepared,
ranging in length from 1 inch to 0.275 inch, in diameter from about 0.2
inch to 0.125 inch, and in frequency from 100 KC to 370 KC. Successive
oscillators differed in length and frequency by about 10%. The faces
normal to the X-axis were given a light coating of Aquadag.

Each sample was coupled to different quartz oscillators until a com-
posite oscillator was found whose frequency fell between the frequencies
of two adjacent quartz oscillators. Equation (2) then becomes a formula
for interpolation, and gives the frequency of the sample with an error
usually less than 1%. Greater precision could be obtained by more care-
ful matching of frequencies and of cross-sections.

As an example of the calculation, consider the sample of beryl with
axis normal to \( c \). Its mass was 1.205 gm., length 0.713 inch. The com-
posite oscillator, formed by joining this with a quartz oscillator of mass
0.515 gm., 0.450 inch long, with a natural frequency of 234,670 cps, had
its resonance at 244,870 cps. Equation (2) then gives 249,240 for the
frequency of the beryl alone. The frequency of the composite oscillator
formed by joining the beryl with a quartz oscillator of mass 0.415 gm.
and frequency 262,630 cps was 253,000 cps. This gives 249,690 cps for the
frequency of the beryl alone, about $\frac{1}{4}\%$ different from the value found with the other oscillator. The mean value, 249,460, gives the velocity, $2f_l = 9.03$ km/sec.

The measurements are summarized in Table 1. The velocity which is tabulated is $2f_l$, with no correction for finite diameter, but the ratio of length to diameter was always greater than three or four. The modulus is obtained from $2f_l = \sqrt{E/\rho}$. The compliance, given in the last column, is the reciprocal of the modulus. All of these results are for extensional vibrations.

**Table 1. Elastic Constants of Extensional Vibrations Determined from Frequencies**

<table>
<thead>
<tr>
<th>Crystal</th>
<th>Density</th>
<th>Velocity Km/sec</th>
<th>Modulus, in $10^{11}$ dyne/cm²</th>
<th>Compliance, in $10^{-13}$ cm²/dyne</th>
</tr>
</thead>
<tbody>
<tr>
<td>Beryl</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>par. c-axis</td>
<td>2.668</td>
<td>9.03</td>
<td>21.8</td>
<td>$s_{33} = 4.60 (4.71)^1$</td>
</tr>
<tr>
<td>perp. c-axis</td>
<td>2.683</td>
<td>9.03</td>
<td>21.9</td>
<td>$s_{11} = 4.57 (4.42)^1$</td>
</tr>
<tr>
<td>Tourmaline, par. c-axis</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>black</td>
<td>3.091</td>
<td>6.88</td>
<td>14.6</td>
<td>$s_{33} = 6.84 (6.24)^2 (6.0)^2$</td>
</tr>
<tr>
<td>yellow</td>
<td>3.028</td>
<td>7.40</td>
<td>16.6</td>
<td>$s_{33} = 6.03$</td>
</tr>
<tr>
<td>pink</td>
<td>3.031</td>
<td>7.47</td>
<td>16.9</td>
<td>$s_{33} = 5.91$</td>
</tr>
<tr>
<td>Topaz</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>a-axis</td>
<td>3.538</td>
<td>8.05</td>
<td>22.9</td>
<td>$s_{33} = 4.36 (4.43)^1$</td>
</tr>
<tr>
<td>b-axis</td>
<td>3.545</td>
<td>9.12</td>
<td>29.5</td>
<td>$s_{22} = 3.38 (3.53)^1$</td>
</tr>
<tr>
<td>c-axis</td>
<td>3.548</td>
<td>8.49</td>
<td>25.6</td>
<td>$s_{22} = 3.91 (3.84)^1$</td>
</tr>
<tr>
<td>Pyrite, a-axis</td>
<td>(5.018)</td>
<td>8.68</td>
<td>37.8</td>
<td>$s_{11} = 2.65 (2.69)^3 (2.89)^3$</td>
</tr>
<tr>
<td>2nd sample</td>
<td>8.72</td>
<td>38.2</td>
<td>38.2</td>
<td>$s_{11} = 2.02$</td>
</tr>
<tr>
<td>Andradite</td>
<td>3.482</td>
<td>8.13</td>
<td>23.0 (orientation)</td>
<td></td>
</tr>
<tr>
<td>Garnet (pyrope)</td>
<td>4.122</td>
<td>7.57</td>
<td>23.6 (undetermined)</td>
<td></td>
</tr>
<tr>
<td>Spodumene</td>
<td>(3.186)</td>
<td>8.96</td>
<td>25.6</td>
<td></td>
</tr>
<tr>
<td>a-axis</td>
<td>7.50</td>
<td>17.9</td>
<td>17.9</td>
<td>$s_{22} = 5.6$</td>
</tr>
<tr>
<td>b-axis</td>
<td>2.51</td>
<td>5.65</td>
<td>8.03</td>
<td></td>
</tr>
</tbody>
</table>

1 Voigt (1928).
2 Osterberg and Cookson (1935).
3 Birch and Bancroft, unpublished.
4 Handbook values, after Berman.

Where possible, values obtained by other methods are given in parentheses; most of these are by Voigt, and show about the same amount of discrepancy as has been found by other observers who have used dynamical methods (Cady, Chapter VI). A difference between Voigt's isothermal values and the present adiabatic ones is to be expected, but this is of the order of a few parts in a thousand.
Table 2 shows results for a group of X-cut quartz rods all nearly 1 inch long, and of approximately square cross-section, about 0.15×0.15 inch. The mean value for 2fl is 5.457 km/sec; with $\rho=2.654$ we obtain $s_{11}=12.64 \times 10^{-13}$ cm$^2$/dyne, in good agreement with the results of other investigators (Cady, 1946, pp. 135–138).

<table>
<thead>
<tr>
<th>Length in inches</th>
<th>Frequency KC</th>
<th>$v=2fl$ km/sec</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.081</td>
<td>99.31</td>
<td>5.453</td>
</tr>
<tr>
<td>1.085</td>
<td>99.00</td>
<td>5.457</td>
</tr>
<tr>
<td>1.058</td>
<td>101.53</td>
<td>5.457</td>
</tr>
<tr>
<td>1.142</td>
<td>94.35</td>
<td>5.473</td>
</tr>
<tr>
<td>1.086</td>
<td>98.91</td>
<td>5.457</td>
</tr>
<tr>
<td>1.086</td>
<td>98.82</td>
<td>5.452</td>
</tr>
<tr>
<td>1.080</td>
<td>98.89</td>
<td>5.486 (poor)</td>
</tr>
<tr>
<td>1.084</td>
<td>98.95</td>
<td>5.449</td>
</tr>
<tr>
<td>1.123</td>
<td>95.54</td>
<td>5.450</td>
</tr>
<tr>
<td>1.086</td>
<td>99.07</td>
<td>5.466</td>
</tr>
<tr>
<td>1.122</td>
<td>95.70</td>
<td>5.455</td>
</tr>
<tr>
<td>1.086</td>
<td>98.95</td>
<td>5.458</td>
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</table>

References