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Ultrasonic Determination of Elastic Constants and Structural Irregularities in Transparent Single Crystals. (Measurements in Sapphire)

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Rotation of the coordinate system describing the trigonal system simplifies the computations involved in relating observed ultrasonic velocities to the elastic constants. The six elastic constants of sapphire are calculated from results of measurements employing two ultrasonic methods: the thickness resonance method and the visibility method. The latter is used to find structural irregularities in the sample as well as their location and approximate size.

Introduction

The use of high ultrasonic frequencies facilitates the experimental determination of the elastic constants of crystals. If the ultrasonic wave length in the sample is small compared with the dimensions of the specimen one can produce plane elastic waves in the crystal. The Christoffel equations which were derived by Green (1839) give the relationship between the velocity of propagation, the density of the sample, the direction of propagation with respect to the coordinate system of the sample, and the elastic constants. For the determination of the elastic constants the measurement of the density of the sample and of the velocity of the ultrasonic waves in a small number of crystallographic directions is necessary. Only a few cuts of the crystal are required.

The Christoffel equations can be applied to any crystalline system. The mathematical formulation resulting from these equations is usually rather involved. The relationship between a measured ultrasonic velocity and the corresponding elastic constants can be obtained in a much simpler form by performing a transformation of the stress tensor pertaining to the special system under consideration. This transformation is outlined here for the trigonal system. The elastic constants are calculated for sapphire using results of velocity measurements obtained from two ultrasonic methods which are also described here. One of the methods is applicable to both transparent and opaque crystals while the other is restricted to transparent samples but offers a possibility to detect structural irregularities in the crystal.

Theory

For the purpose of this paper it is assumed that for all experiments Hooke's law is valid which, under adiabatic conditions, can be written

$$\left.\begin{aligned} S_{ij} &= s_{ijkl}T_{kl} \\ T_{ij} &= c_{ijkl}S_{kl} \end{aligned}\right\} \quad \left.\begin{aligned} &i, j, k, l = 1, 2, 3 \\ &S_{ij} = S_{ji};\ T_{ij} = T_{ji} \end{aligned}\right\}. \qquad (1)$$

Equation (1) can be written

$$\left.\begin{aligned} S_p &= s_{pq}T_q \\ T_p &= c_{pq}S_q \end{aligned}\right\} \quad p, q = 1, 2, 3, \ldots, 6, \qquad (2)$$

if the suffixes $ij, kl = 11, 22, 33, 23, 13, 12$ are replaced by $p, q = 1, 2, 3, 4, 5, 6$, respectively. According to the notation of Voigt (1928) the C_{pq} are called the elastic constants while the s_{pq} are the elastic moduli.

The Christoffel equations are usually employed to evaluate the elastic constants from the experimental data. Their application is based on the fact that with an elastic wave propagated in an anisotropic medium there are associated three independent, mutually orthogonal displacement vectors $\mathbf{D}$ which are functions of the wave vector $\mathbf{k}$ whose direction is perpendicular to the planes of constant phase of the wave. In general the three $\mathbf{D}$ belong to three different waves which are propagated in the direction of $\mathbf{k}$ with three different velocities. If one of the three $\mathbf{D}$ is parallel to $\mathbf{k}$ one purely longitudinal and two purely transverse waves will result. In most cases, however, the waves will contain longitudinal and shear components. If the expression 'longitudinal' wave is used in the following, it will designate a 'predominantly longitudinal' wave; the same holds for 'shear' waves.

Let the Cartesian coordinate system of the anisotropic material be fixed such that the propagation vector $\mathbf{k}$ of the elastic wave has the direction cosines l, m, n. The three possible velocities are then the roots of the cubic equation (Christoffel equation)

$$\begin{vmatrix} \Phi_{11}-\varrho V^2 & \Phi_{12} & \Phi_{13} \\ \Phi_{12} & \Phi_{22}-\varrho V^2 & \Phi_{23} \\ \Phi_{13} & \Phi_{23} & \Phi_{33}-\varrho V^2 \end{vmatrix} = 0, \qquad (3)$$

where ϱ is the density. The Φ_{ab} are defined by

$$\Phi_{ab} = l^2C_{1a1b}+m^2C_{2a2b}+n^2C_{3a3b}+mn(C_{2a3b}+C_{3a2b}) + nl(C_{3a1b}+C_{1a3b})+ml(C_{1a2b}+C_{2a1b})\,. \qquad (4)$$

The elastic constants C_{ijkl} in equation (4) can be written in standard form by converting them to the corresponding C_{pq}. It is obvious from equations (3) and (4) that the form of the solution of equation (3) will be rather involved unless two of the direction cosines are zero. Fortunately, some of the C_{pq} vanish, and the non-zero terms are usually written in the form of a matrix for a given crystal group. For the trigonal system this matrix becomes

$$\begin{bmatrix} C_{11} & C_{12} & C_{13} & C_{14} & 0 & 0 \\ C_{12} & C_{11} & C_{13} & -C_{14} & 0 & 0 \\ C_{13} & C_{13} & C_{33} & 0 & 0 & 0 \\ C_{14} & -C_{14} & 0 & C_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & C_{44} & C_{14} \\ 0 & 0 & 0 & 0 & C_{14} & C_{66} \end{bmatrix} \tag{5}$$

where $C_{66} = \frac{1}{2}(C_{11}-C_{12})$.

Substituting the appropriate C_{pq} from equation (5) into equation (4) one obtains quite readily expressions for the six Φ_{ab}. Bhimasenachar (1945) finds solutions for the Christoffel equations for some specific directions of $\mathbf{k}$ for the trigonal system in which the Cartesian coordinate system is placed in such a manner that the Z axis coincides with the trigonal axis while the X axis corresponds to the a_1 axis. Quite obviously, any solution of equation (3) will contain terms in $\varrho^3 V^6$, $\varrho^2 V^4$, and ϱV^2 whose coefficients are various combinations of C_{pq}. The computation involved in separating the six elastic constants is usually quite cumbersome, particularly in the case of coupled longitudinal and shear modes.

In order to simplify the calculation of the elastic constants it is advantageous to perform a rotation of the entire Cartesian coordinate system such that the Z axis of the rotated system is always in the direction of the wave propagation vector $\mathbf{k}$. Let the new Z axis be called the Z' axis, and the new coordinate system the $X'Y'Z'$ system. Depending on the direction of $\mathbf{k}$ there will be a set of direction cosines relating the two systems, expressed by the following scheme

	X_1'	X_2'	X_3'
X_1	a_{xx}	a_{xy}	a_{xz}
X_2	a_{yx}	a_{yy}	a_{yz}
X_3	a_{zx}	a_{zy}	a_{zz}

(6)

An elastic wave travelling in the direction of $\mathbf{k}$ has associated with it one longitudinal and two shear waves which may be mixed waves. By conventional definition—see Sokolnikoff (1956)—the constants C'_{33} and C'_{44} refer to the longitudinal and the shear waves, respectively. These constants will be combinations of various unprimed C_{pq}. Since one finds experimentally only the velocity of the longitudinal and that of one of the two shear waves in a given direction one can substitute the measured values of V into

$$\varrho V_L^2 = C'_{33} \quad \text{or} \quad \varrho V_S^2 = C'_{44} \,. \tag{7}$$

In order to be able to relate any observed velocity to the unprimed C_{pq} which are to be determined one notes that equation (5) is a tensor of rank 4 which can be transformed to a new Cartesian coordinate system $(X'Y'Z')$ by the equation

$$C'_{rstu} = \frac{\partial x'_r}{\partial x_i}\frac{\partial x'_s}{\partial x_j}\frac{\partial x'_t}{\partial x_k}\frac{\partial x'_u}{\partial x_l} C_{ijkl}\,, \tag{8}$$

where $i, j, k, l = 1, 2, 3$ and $r, s, t, u = 1, 2, 3$.

The $\frac{\partial x'_r}{\partial x_i} \cdots \frac{\partial x'_u}{\partial x_l}$ are the direction cosines of (6). Observing that some of the C_{ijkl} are equal to zero in the trigonal system, one finds that for C'_{3333} only 12 terms in C_{ijkl} remain to be summed. These terms, if written in the 2-suffix system, have suffixes which give their actual positions in the array (5). Replacing these suffixes by those required by the matrix of the trigonal system (e.g. $C_{56} = -C_{24} = C_{14}$) and rearranging them one obtains for a longitudinal elastic wave in any direction of $\mathbf{k}$

$$\left.\begin{aligned} C'_{33} = C_{11}(1-a_{zz}^2)^2 + C_{33}a_{zz}^4 + (4C_{44}+2C_{13})(1-a_{zz}^2)a_{zz}^2 \\ +4C_{14}(3a_{xz}^2-a_{yz}^2)a_{yz}a_{zz}\,. \end{aligned}\right\} \tag{9}$$

By an analogous procedure one finds

$$\left.\begin{aligned} \mathrm{C}'_{44} = {} & \mathrm{C}_{11}(a_{xy}^2a_{xz}^2 + a_{yy}^2a_{yz}^2) + 2\,\mathrm{C}_{12}a_{xy}a_{xz}a_{yy}a_{yz} \\ & +2\,\mathrm{C}_{13}[a_{zy}a_{zz}(a_{xy}a_{xz}+a_{yy}a_{yz})] + \\ & 2\,\mathrm{C}_{14}[2a_{xy}a_{xz}(a_{yy}a_{zz}+a_{yz}a_{zy}) + (a_{xy}^2a_{yz}a_{zz} \\ & \quad +a_{xy}^2a_{yy}a_{zy} - a_{yy}^2a_{yz}a_{zz} - a_{yz}^2a_{yy}a_{zy})] \\ & +\mathrm{C}_{33}(a_{zy}^2a_{zz}^2) + \mathrm{C}_{44}[(a_{yy}a_{zz}+a_{yz}a_{zy})^2 \\ & \quad + (a_{xy}a_{zz}+a_{xz}a_{zy})^2] \\ & +\mathrm{C}_{66}(a_{xy}a_{yz}+a_{xz}a_{yy})^2\,. \end{aligned}\right\} \tag{10}$$

It should be noted that only one C'_{33} is possible for a given direction while two C'_{44} can be obtained. This is evident from the fact that in the 4-suffix system C'_{44} can be expressed in four different ways, i.e. $rstu$ = 2233, 2323, 3322, 3232. These two sets of two equivalent arrangements result in two slightly different formulas for C'_{44}. Only one form is given in equation (10), the other form is found by rotating the $X'Y'Z'$ system around Z' until the Y' axis has taken the place of the X' axis. This procedure changes the values of some of the direction cosines in (6) and gives the second form of C'_{44}. The direction cosines occurring in equation (9) are not affected by such a rotation.

Application

The relations given above are applied to three blocks of synthetic single crystal sapphire which were prepared by the Linde Air Products Company of New York. The normals to the plane-parallel faces make the following angles with the XYZ coordinate system. (φ is the angle between the projection of the normal in the XY plane and the X axis, and θ the angle between the normal and the Z axis.)

Block	Direction of normal	φ	θ
I	X	0	90
I	Y	90	90
I	Z	0	0
II	A	0	135
II	B	0	45
III	A	90	135
III	B	90	45

(11)

Placing the Z' axis in the direction of the normal, one obtains a set of direction cosines which is substituted into equations (9) and (10) to yield expressions for the C′ in terms of C_{pq}. Some of the results are given below.

$$\left.\begin{array}{ll} \mathrm{I}\,X: & C'_{33} = C_{11};\ C'_{44} = C_{44};\ C'_{44} = C_{66}\,. \\ \mathrm{I}\,Z: & C'_{33} = C_{33};\ C'_{44} = C_{44}\,. \\ \mathrm{II}\,A: & C'_{33} = \tfrac{1}{4}(C_{11}+C_{33}+4\,C_{44}+2\,C_{13}); \\ & C'_{44} = \tfrac{1}{2}(C_{44}+C_{66}); \\ & C'_{44} = \tfrac{1}{4}(C_{11}+C_{33}-2\,C_{13})\,. \end{array}\right\} \qquad (12)$$

Similar expressions are obtained for other directions of the normal. Replacing the C′ in above expressions by ϱV^2, where V is the ultrasonic velocity measured in the appropriate directions of **k**, one can easily find all the elastic constants. Only the constants C_{11}, C_{33}, and C_{44} can be found directly from measurements in the X or Y and the Z direction.

Experimental methods

The elastic constants of a crystal can be determined with a number of static and dynamic methods. Hearmon (1946), (1956) describes in detail their applicabilities and limitations. The size of the samples available allowed the use of two ultrasonic methods which were found to be very reliable and accurate: The thickness resonance method and the visibility method.

Thickness resonance method

If an ultrasonic wave is transmitted into a sample with parallel faces one finds that resonance of the sample can be observed at various frequencies depending on the dimensions of the sample. Ultrasonic energy is transmitted into the sample by attaching a quartz transducer to the flat surface of the crystal whose normal then corresponds to the direction of **k**. A thin film of silicon grease or heavy oil between the transducer and the crystal will provide sufficient acoustic coupling in most cases. The transducer is driven by a radio frequency oscillator whose frequency is variable. First one finds a frequency at which maximum transmission through the sample occurs, then one varies the frequency until another maximum is observed. If a longitudinal elastic wave causes the occurrence of both maxima in such a manner that the number of half wave lengths set up between the parallel faces of the crystal by the standing wave produced at the two frequencies has changed by exactly one due to the change in frequency, one can find the total number of half wave lengths present in the specimen for each maximum. This can be seen if one considers that the velocity is constant in a given direction. Therefore, only at certain frequencies will it be possible to produce an elastic wave whose wave length is such that $n\lambda^*/2 = D$ where n is any integer, and D is the distance between the parallel faces of the crystal. It follows that the successive conditions for resonance can be expressed

$$\frac{V_L}{D} = \frac{F_1}{n/2} = \frac{F_2}{(n+1)/2} = \frac{F_3}{(n+2)/2} = \ldots, \qquad (13)$$

where F_i are the resonance frequencies and $F_1 < F_2 < F_3 < \ldots$. From equation (13) one can find n, $n+1$, ..., and the velocity. It is advisable to find more than two resonance frequencies for the calculation of V_L, particularly when n is greater than about 10.

Resonance frequencies can be determined by optical effects. If the sample is transparent it can be placed in the path of collimated light in such a fashion that **k** is perpendicular to the direction of light propagation. A standing wave, which is set up at a resonance frequency, will act as an ultrasonic grating for the collimated light and will produce a strong diffraction pattern. These patterns, first discovered by Lucas & Biquard (1932), can be observed on a screen with an optical arrangement shown in Fig. 1. Vedam (1950) used this method for experiments on optical glasses.

Because of the small radiation damping in air the resonance is very sharp; the diffraction pattern disappears for very small deviations from the resonance frequencies which can therefore be determined with an accuracy of better than 0·1%.

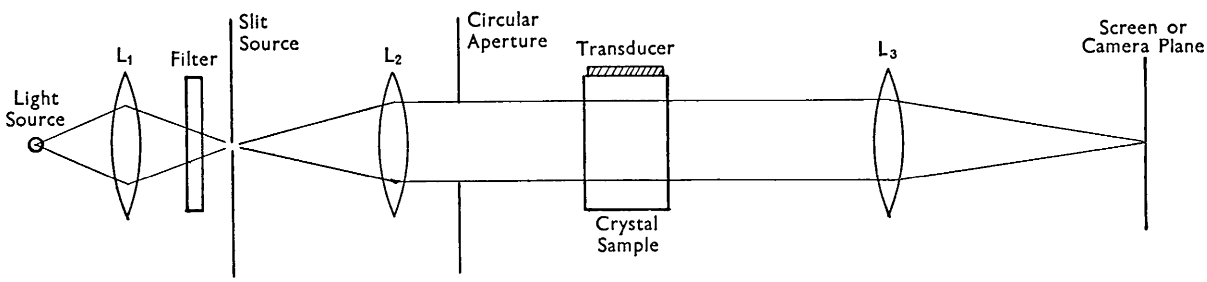


Fig. 1. Optical arrangement for thickness resonance method.

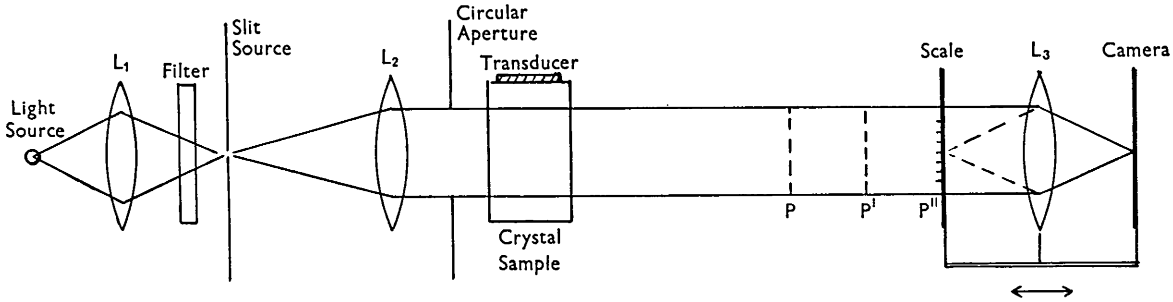


Fig. 2. Optical arrangement for visibility method.

It is also possible to immerse the crystal partly in a liquid in which a diffraction pattern will be observed if maximum transmission through the specimen occurs. This principle was applied extensively by Bhagavantam (1946) and Bhimasenachar (1950) for measurements of crystal plates. The transmission becomes maximum at the resonance frequency of the thickness vibrations. However, in this case there is considerable radiation damping caused by the liquid which decreases the sharpness of the resonance. The diffraction pattern does not vanish as rapidly with a slight change in frequency; the determination of resonance frequencies loses in accuracy. This method can be applied to opaque solids in which case, however, much higher accuracies may be obtained by vibrating the specimen in air and by determining the resonance frequencies by electronic instead of optical methods.

Longitudinal waves are usually quite easily excited and observed; shear waves are sometimes rather difficult to measure with this method since the diffraction patterns produced at their respective resonance frequencies are much weaker than those of the longitudinal waves. It is therefore not difficult to decide whether an observed maximum transmission is to be assigned to the series of resonance frequencies due to longitudinal or shear waves.

Visibility method

In this method use is made of the fact that an ultrasonic wave in a transparent substance acts very much like a ruled grating; the ultrasonic waves are made visible and their 'grating constants' can be measured. From such measurements one is able to calculate the velocity of propagation of the wave producing the grating. This method, developed by Hiedemann *et al.* (1939), is one of the most powerful known methods within its range of applicability (transparency, etc.); it yields very accurate values of velocities and is thus well suited to find the elastic constants of transparent crystals. It also reveals some information about the sample which is not obtainable with other ultrasonic methods.

The necessary optical arrangement is shown in Fig. 2. Ultrasonic energy is transmitted into the specimen in the usual manner. A standing longitudinal or transverse wave is set up in the sample and acts as diffraction grating for the monochromatic light collimated by lens L_2. This arrangement produces an interference pattern at the planes $P, P', \ldots$ which are equally spaced along the optic axis. The periodicity of the visibility of the ultrasonic grating is given by a relation by Nath (1936) and Nomoto (1936) very similar to that by Lord Rayleigh (1881) for the periodicity of ruled optical gratings.

The interference patterns in their simplest form consist of a series of lines whose spacings are equal to the distance between the nodes or antinodes of the standing wave in the sample. If, e.g., the wave length of the elastic wave in the specimen is 1 mm., the lines produced at $P, P', \ldots$ are 0·5 mm. apart. One can observe and measure these lines either with a travelling microscope focused on one of the image planes or one can photograph directly a section of the planes containing the interference lines. Depending on the dimensions of the illuminated sections of the crystal and on the wave length of the standing wave one can observe from 10 to more than 50 lines. Placing a transparent scale in the plane to be photographed eliminates a number of possible errors in relating distances measured on the enlarged photograph to actual distances on the film negative.

The determination of the desired elastic constants is done in the following way. One measures the distance between a number of lines on the photograph (with the correct scale appearing in the picture) which yields the ultrasonic wave length in the crystal, and with a knowledge of the excitation frequency used, one can find the velocity. The velocity is that of either a longitudinal or shear wave. The spacing of the lines gives an indication of what kind of standing wave is set up in the sample. At about the same frequency shear waves, having a lower velocity, produce lines more closely spaced than those due to longitudinal waves. Fig. 3 is part of a photograph of a standing longitudinal wave in the Z direction in sapphire at a frequency of 9·006 Mc. Measuring the distance between any two lines with the scale visible in the photograph, and knowing that the distance between adjacent lines equals one half wave length, one finds the value of the longitudinal velocity to be 11,215 m.sec.$^{-1}$. The density of the sample is 3·988 g.cm.$^{-3}$. From equation (7) one obtains $C'_{33} = 50{\cdot}2 \times 10^{11}$ dynes cm.$^{-2}$,

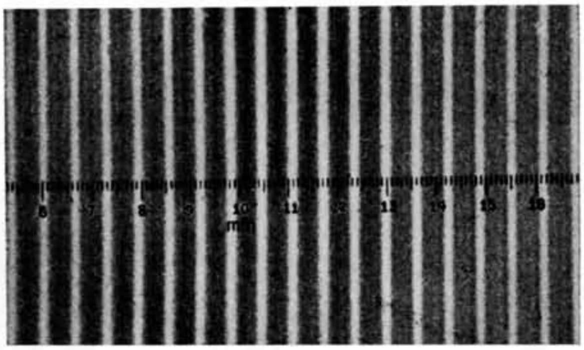


Fig. 3. Regular interference lines in Z direction.

where $C'_{33} = C_{33}$ for the Z direction. The rest of the elastic constants is computed in a similar manner. The definition of the visible lines in the photographs is increased by using polarized light.

Numerical values of constants

At least six measurements are required in both methods for the calculation of the six constants. With the thickness resonance method one finds various series of resonance frequencies corresponding to standing waves in the crystallographic directions outlined in (11). The respective velocities are found from equation (13). In the visibility method the wave lengths of standing waves in different directions are measured directly, and the respective velocities are found from $V = f\lambda^*$.

The numerical values of the six elastic constants are then calculated by substituting the measured velocities into the appropriate equations samples of which are given in equation (12). The elastic constants of synthetic sapphire are found to be:

$$\begin{array}{ll} C_{11} = 49{\cdot}6 & C_{12} = 10{\cdot}9 \\ C_{33} = 50{\cdot}2 & C_{13} = 4{\cdot}8 \\ C_{44} = 20{\cdot}6 & C_{14} = 3{\cdot}8 \end{array}$$

In units of 10^{11} dynes cm.$^{-2}$.

These values do not agree too well with those reported by Sundara Rao (1949) and Bhimasenachar (1950). Both authors employ a method in which the ultrasonic transmission through a thin sapphire disk is measured. A wedge-shaped quartz transducer—the method of Bhagavantam (1944)—is used in their experiments. Their experiments were repeated and it was found that there exists a series of limited frequency ranges rather than a series of peak frequencies at which maximum transmission occurs. An obvious reason for the difficulty to obtain sharp resonance peaks with thin plates is the following: The sharpness of the thickness resonance decreases appreciably if there exist even slight variations in the thickness of the plate. It is difficult to obtain the homogeneity of the samples required for sharp resonance in thin plates.

Calculations show that the velocities obtained by the methods described in this paper fall within the range of error inherent in the wedge method; this margin of error is quite large, and the value of C_{33} may fluctuate between 49 and 56×10^{11} dynes cm.$^{-2}$. The discrepancy between the values of Sundara Rao (1949), 50·6, and Bhimasenachar (1950), 56·3, falls within the observed range of error. On the other hand, both the thickness resonance and the visibility methods yield values of C_{33} accurate to within less than 0·5%.

Structural irregularities

It is usually assumed that the ultrasonic velocity in a particular direction is uniform, and a calculation of the velocity according to the results of most methods is actually based on that assumption, or what amounts to the same end result, one finds an average ultrasonic velocity in a certain crystallographic direction. Therefore, one has to use other methods to prove or disprove the assumption of uniformity. Here a special advantage of the visibility method becomes apparent. Consider what will happen if in the single crystal sample there should be a layer of irregularity. Under these conditions it will still be possible to accommodate an integral number of half wave lengths provided the character of the standing wave is not completely destroyed. Observation of a standing elastic wave does therefore not necessarily imply that the specimen has a uniform structure throughout. Fig. 4 illustrates this

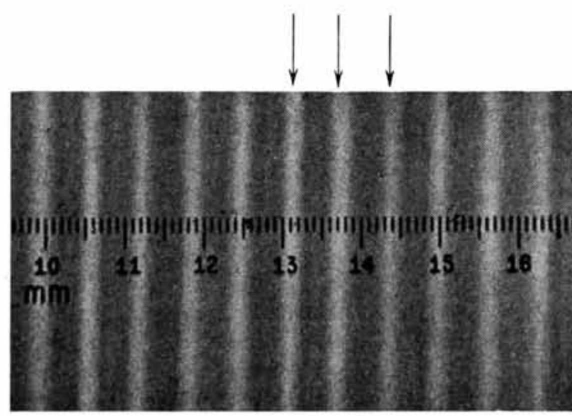
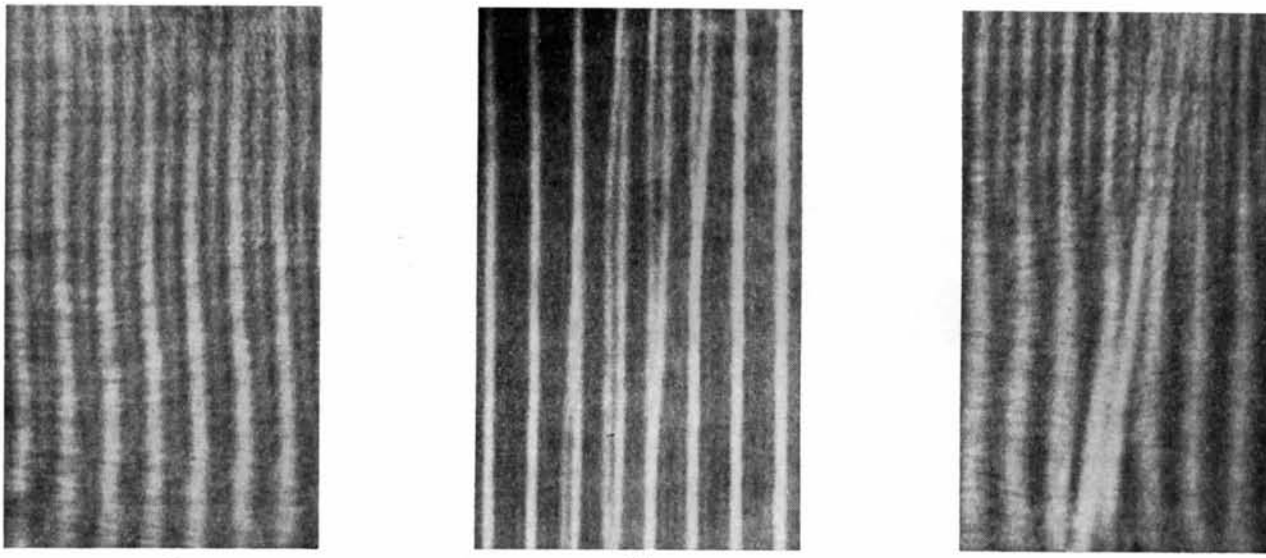


Fig. 4. Irregular spacing of interference lines.

point. Closer inspection of the lines through 13·1, 13·7, and 14·4 reveals that they are not evenly spaced. The spacing of the first two lines is smaller than the average, and the next two lines are spaced wider. This shows that the velocity in that region varies and differs from the average velocity in the rest of the specimen along the same direction. This phenomenon gives an indication of the average velocity in a small slice of the crystal whose thickness is limited by the spacing between the interference lines. By increasing the frequency it is possible to narrow this slice. The limit of this process is essentially set by the width of the



(a) (b) (c)

Fig. 5. Structural irregularities in sapphire.

observed lines. By rotating the sample around the axis of ultrasonic propagation it is possible to find also the approximate lateral dimensions of the region of irregularity. The irregularities may have different origins; polycrystallinity, variations in density, etc. may be the cause.

Other structural irregularities are seen in Fig. 5. The sensitivity in detecting small inhomogeneities is increased if a greater number of lines per unit length is observed. In order to obtain more lines without increasing the frequency one moves the whole assembly camera, L_3, and scale (see Fig. 2) along the optic axis. At various distances between the planes $P, P', \ldots$ the interference of diffraction orders is such that the number of visible lines doubles as was pointed out by Hiedemann & Schreuer (1937). Fig. 5(a) is a photograph taken under these conditions. It shows how the lines bend and become blurred in some sections. Examination of the sapphire sample under polarized light shows that the specimen is irregular in the region in question, and since the wave length of an elastic wave is a function of the orientation of the crystal one can expect shifts in the visible lines. Diverging and discontinuous lines in Figs. 5(b) and 5(c) can be used to locate similar regions of irregularities.

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