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A Method for Determining the Elastic Constants of a Cubic Crystal from Velocity Measurements in a Single Arbitrary Direction; Application to $SrTiO_3$

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Three independent velocities of sound can be measured along any direction of propagation in a cubic crystal except the [100] and [111] directions. These three velocities suffice to determine the three elastic constants and for the [110] direction, the calculation of these constants is easy. For all other directions, the calculation is more difficult; the only existing method appears to be a perturbation technique developed by Neighbours.

The present paper presents a method using exact equations and an iterative procedure to solve these equations and to calculate both the elastic constants and their standard deviations from the sound velocities and their standard deviations. The method is illustrated with new data on $SrTiO_3$ which give $c_{11}=3.156\pm0.027$, $c_{12}=1.027\pm0.027$, $c_{44}=1.215\pm0.006\times10^{12}$ dynes/cm^2 at 25 °C. The importance of including covariance terms in calculations of the standard deviations is emphasized.

1. Introduction

The determination of the elastic constants of single crystals from measurements of the velocity of sound is an extensive and active field of research and several survey papers exist [*1, 2, 3, 4*].[1] For any direction in a single crystal three types of sound wave may be propagated: one quasi-longitudinal and two quasi-transverse waves. The three corresponding velocities are the roots of a cubic equation, sometimes called Christoffel's equation, whose coefficients are complicated functions of the elastic constants and the direction cosines for the direction of propagation of the sound. In the case of a cubic crystal, there are only three independent elastic constants so that velocity measurements in a single direction suffice to completely determine the elastic constants provided that no two velocities are required to be equal by crystal symmetry. Such equality is required for the [100] and [111] directions so that measurements in one of these directions alone do not provide sufficient information to determine the three elastic constants. It may happen that for some other direction two of the velocities are equal; the three velocities are still independent quantities, however, and measurements in such a direction would provide sufficient information to calculate the three elastic constants. We assume that the three velocities v_1, v_2, v_3, and their standard deviations σ_1, σ_2, σ_3, have been measured for some direction which is specified by direction cosines l, m, n and which does not coincide with or closely neighbor [100] or [111]. We seek to calculate the three independent elastic constants c_{11}, c_{12}, c_{44} and their standard deviations σ_{11}, σ_{12}, σ_{44}. The theory leads to a sixth degree algebraic equation of which c_{11} must be a root. It may occur that more than one of the roots of this equation are of reasonable magnitude so that some test is needed to distinguish which of the roots is c_{11}. The direction of polarization of the quasi-transverse waves provides such a test and we therefore assume that the orientation of the transducer exciting each of the two quasi-transverse waves was also determined.

One would usually prefer to use the [110] direction for which the calculations are easy and well known and for which the present method is unnecessary. However, single crystals of many substances are available only in very limited sizes and shapes and it may occur that the only available crystals do not permit measurement along [110]. Also, even if [110] is accessible for measurement, it may be desired to check the results by measurements in other directions.

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[1] Italicized figures in brackets indicate the literature references at the end of this paper.

Neighbours and his collaborators [*5, 6, 7*], following a beginning by Ahrenberg [*8*], have developed an approximation method for calculating elastic constants from wave velocities and have applied it to the case of cubic crystals as well as several other crystal systems. In Neighbours' method, the equations relating the velocities and the elastic constants are expanded into infinite series. The first term of each equation is a simple linear combination of elastic constants and the first step in his self-consistent calculation is to solve for the elastic constants ignoring all other terms. The values so obtained are used to calculate the largest of the remaining terms of the infinite series and a second set of values of the elastic constants is then calculated considering only the elastic constants of the first term as variables. This process is repeated as often as necessary to obtain the desired degree of accuracy. Successive sets of elastic constants calculated in this manner converge to a set which satisfies the chosen finite portions of Neighbours' expanded form of the velocity equations.

Presumably the next order terms could be calculated if greater accuracy were desired, but they apparently have not been given. The present method which uses exact equations thus provides a desirable alternative to Neighbours' method. The propagation-of-error theory could presumably be applied to Neighbours' method to calculate standard deviations, but this has apparently not been worked out. The present method includes such a calculation and this is worthy of note because the calculation involves quantities which are not statistically independent and serious errors can arise if the elementary propagation-of-error equations, which do not include covariance terms, are used. Any comparison of Neighbours' method with the present work should note the great utility and generality of the former which can be applied to crystals of any symmetry (if sufficient measurements are available) while the latter is strictly limited to cubic crystals.

2. Equations for Calculating Elastic Constants

The equations relating elastic constants to wave velocities are derived in many places; see, for example, Kolsky [*9*] for a treatment in conventional (matrix) notation and Farnell [*10*] for a brief sketch in tensor notation. The resulting secular equation can be written as an equation involving a 3 × 3 determinant using Farnell's notation as

$$|\Gamma_{jk}-\delta_{jk}x|=0 \tag{1}$$

where

$$x=\rho v^2 \tag{2}$$

$$\rho=\text{density},$$

$$v=\text{velocity},$$

and

$$\Gamma_{jk}=\frac{1}{2}\sum_{i,l}\alpha_i\alpha_l(c_{ijkl}+c_{ijlk}) \tag{3}$$

In the last expression, the α_i are the direction cosines for the direction of propagation and the c_{ijkl} are the elastic constants; both are referred to the crystal axes. Assuming cubic symmetry, writing l, m, n for the direction cosines and using the conventional matrix notation for elastic constants, the Γ_{jk} become

$$\Gamma_{11}=c_{11}l^2+c_{44}(m^2+n^2) \tag{4}$$

$$\Gamma_{22}=c_{11}m^2+c_{44}(l^2+n^2) \tag{5}$$

$$\Gamma_{33}=c_{11}n^2+c_{44}(l^2+m^2) \tag{6}$$

$$\Gamma_{12}=\Gamma_{21}=(c_{12}+c_{44})lm, \tag{7}$$

$$\Gamma_{13}=\Gamma_{31}=(c_{12}+c_{44})ln, \tag{8}$$

and

$$\Gamma_{23}=\Gamma_{32}=(c_{12}+c_{44})mn. \tag{9}$$

These values can be substituted into the secular equation to give a cubic equation in x. We assume that for a given direction (l, m, n) the three velocities have been measured and the three corresponding values x_1, x_2, x_3, computed. Then for this direction the cubic equation obtained from the secular equation must factor into

$$(x-x_1)(x-x_2)(x-x_3)=0. \tag{10}$$

When this factored equation is multiplied out and the coefficients of each power of x equated to the coefficient of the same power in the secular equation three simultaneous equations are obtained. To simplify these, let

$$\alpha=c_{11}, \tag{11}$$

$$\beta=c_{44}, \tag{12}$$

$$\gamma=c_{12}+c_{44}, \tag{13}$$

$$u=x_1+x_2+x_3, \tag{14}$$

$$v=x_1x_2+x_1x_3+x_2x_3, \tag{15}$$

and

$$w=x_1x_2x_3. \tag{16}$$

The three equations are

$$u=\alpha+2\beta, \tag{17}$$

$$\begin{aligned} v=&[\alpha l^2+\beta(l^2+m^2)][\alpha m^2+\beta(l^2+n^2)]\\ &+[\alpha l^2+\beta(l^2+m^2)][\alpha n^2+\beta(l^2+m^2)]\\ &+[\alpha m^2+\beta(l^2+n^2)][\alpha n^2+\beta(l^2+m^2)]\\ &-\gamma^2(l^2m^2+l^2n^2+m^2n^2), \end{aligned} \tag{18}$$

and

$$\begin{aligned} w=&[\alpha l^2+\beta(m^2+n^2)][\alpha m^2+\beta(l^2+n^2)][\alpha n^2+\beta(l^2+m^2)]\\ &+2\gamma^3l^2m^2n^2-\gamma^2\{l^2m^2[\alpha n^2+\beta(l^2+m^2)]\\ &+l^2n^2[\alpha m^2+\beta(l^2+n^2)]+m^2n^2[\alpha l^2+\beta(m^2+n^2)]\}. \end{aligned} \tag{19}$$

The problem is to solve for α, β, and γ from a known set of values of u, v, w, l, m, and n. The procedure is to use eq (17) to eliminate β from eqs (18) and (19). Then use (18) to eliminate the γ^2 term from (19). This leaves one equation, derived from (18), which can be solved for γ^2 and one equation, derived from (19), which can be solved for γ^3. Cubing the first of these two equations and squaring the second allows the elimination of γ and gives a 6th degree equation in α. The coefficients in this equation are very long expressions when written out in full and it is much more convenient to define various functions of the starting quantities (l, m, n, u, v, w) and so simplify the algebraic manipulations. We thus define

$$l_1=1-l^2, \tag{20}$$

$$m_1=1-m^2, \tag{21}$$

$$n_1=1-n^2, \tag{22}$$

$$l_2=3l^2-1, \tag{23}$$

$$m_2=3m^2-1, \tag{24}$$

$$n_2=3n^2-1, \tag{25}$$

$$e=l^2m^2+l^2n^2+m^2n^2, \tag{26}$$

$$f=l^2m^2n_2+l^2n^2m_2+m^2n^2l_2, \tag{27}$$

$$g=l_2m_2+l_2n_2+m_2n_2, \tag{28}$$

$$h=l_2m_2n_1+l_2n_2m_1+m_2n_2l_1, \tag{29}$$

$$j = l_2m_1 + l_1m_2 + l_2n_1 + l_1n_2 + m_2n_1 + m_1n_2, \tag{30}$$

$$k = l^2m^2n_1 + l^2n^2m_1 + m^2n^2l_1, \tag{31}$$

$$p = l_2m_1n_1 + l_1m_2n_1 + l_1m_1n_2, \tag{32}$$

$$q = l_1m_1 + l_1n_1 + m_1n_1, \tag{33}$$

$$r = 2l^2m^2n^2, \tag{34}$$

$$s = l_1m_1n_1, \tag{35}$$

$$s_1 = l_2m_2n_2, \tag{36}$$

$$g_1 = gf/e - s_1, \tag{37}$$

$$h_1 = (ugk + ujf)/e - hu, \tag{38}$$

$$j_1 = (u^2jk + u^2qf - 4vf)/e - u^2p, \tag{39}$$

$$k_1 = uk(u^2q - 4v)/e - u^3s + 8w, \tag{40}$$

and

$$p_1 = u^2q - 4v. \tag{41}$$

When (17) is used to eliminate β, eq (18) becomes

$$v = \alpha^2g/4 + \alpha uj/4 + u^2q/4 - \gamma^2e, \tag{42}$$

and eq (19) becomes

$$w = \alpha^3s_1/8 + \alpha^2uh/8 + \alpha u^2p/8 + u^3s/8 + r\gamma^3 - \gamma^2(\alpha f + uk)/2. \tag{43}$$

Substituting for γ^2 from (42) into (43) gives

$$w = \alpha^3(s_1e - gf)/8e + \alpha^2(ueh - ugk - ujf)/8e + \alpha(u^2ep - u^2jk - u^2qf + 4vf)/8e + (u^3es - u^3kq + 4uvk)/8e + r\gamma^3. \tag{44}$$

Computing $64r^2\gamma^6/e^3$ from (42) and equating to the same quantity computed from (44) gives

$$a_6\alpha^6 + a_5\alpha^5 + a_4\alpha^4 + a_3\alpha^3 + a_2\alpha^2 + a_1\alpha + a_0 = 0 \tag{45}$$

where

$$a_0 = r^2p_1^3/e^3 - k_1^2, \tag{46}$$

$$a_1 = 3ur^2jp_1^2/e^3 - 2j_1k_1, \tag{47}$$

$$a_2 = 3r^2(gp_1^2 + u^2j^2p_1)/e^3 - 2h_1k_1 - j_1^2, \tag{48}$$

$$a_3 = r^2(6ugjp_1 + u^3j^3)/e^3 - 2(g_1k_1 + h_1j_1), \tag{49}$$

$$a_4 = 3r^2(u^2gj^2 + g^2p_1)/e^3 - (2g_1j_1 + h_1^2), \tag{50}$$

$$a_5 = 3ur^2g^2j/e^3 - 2g_1h_1, \tag{51}$$

and

$$a_6 = r^2g^3/e^3 - g_1^2. \tag{52}$$

The procedure for determining the elastic constants is thus as follows: Starting with the density, ρ, the velocities v_1, v_2, v_3 and the direction cosines l, m, n first compute x_1, x_2, x_3 from (2), next compute u, v, w from eqs (14) through (16), next compute the quantities defined in eqs (20) through (41), then compute the coefficients given by eqs (46) through (52). Using these coefficients plot eq (45) to determine the real, positive roots in the region of physical interest; if there is more than one such root choose the correct one, which is $\alpha = c_{11}$, as described below. Equation (45) can be plotted and the chosen root determined as accurately as desired by routine automatic computer techniques to save laborious hand computation. Then compute c_{44} from

$$c_{44} = (u - c_{11})/2. \tag{53}$$

Use eq (42) to compute $\gamma^2=(c_{12}+c_{44})^2$ and obtain γ. The sign of the square root is determined by the γ^3 term in eq (43). Then compute c_{12} from

$$c_{12}=\gamma-c_{44}. \tag{54}$$

The only ambiguity which arises in this calculation results from the fact that more than one physically reasonable root of eq (45) may occur and each such root may lead to a set of three elastic constants, none of which can be ruled out by the inequalities of Alers and Neighbours [*11*] or by any general physical argument. In this case, one can take one set and compute the polarization of each of the two quasi-transverse waves (the procedure for computing the polarization is given, for example, by Farnell [*10*]) and compare with the polarization of the transducer used to excite the waves. The results should agree for only one set of elastic constants so that the correct choice of root for c_{11} can be made in this way. A second way is to measure velocities in a second direction in the crystal and compare the elastic constants so determined. Although more than one set of elastic constants may give the correct velocities for one direction (but not the correct polarizations) only one set should give the correct velocities for both directions. This second way of choosing c_{11} avoids the need to consider the direction of polarization.

3. Equations for Computing Standard Deviations of the Elastic Constants

It is assumed that uncertainty in the density and the direction cosines may be ignored and that the principal uncertainty in the data is expressed by the three statistically independent standard deviations σ_1, σ_2, σ_3 of the velocities v_1, v_2, v_3. It is easiest to divide the calculation of the standard deviations σ_{11}, σ_{12}, σ_{44} (of c_{11}, c_{12}, c_{44} respectively) into two parts. First, propagation-of-error theory is used to calculate the variances and covariances of u, v, w. Second, these results are then used to calculate σ_{11}, σ_{12}, and σ_{13}.

The following result [12] from propagation-of-error theory is needed: Let x and y be statistically independent variables with known variances (variance=square of standard deviation). Let u and v be defined as functions of x and y and let F be defined as a function of u and v. Then

$$\sigma_F^2=\left(\frac{\partial F}{\partial u}\right)^2\sigma_u^2+\left(\frac{\partial F}{\partial v}\right)^2\sigma_v^2+2\left(\frac{\partial F}{\partial u}\right)\left(\frac{\partial F}{\partial v}\right)\operatorname{cov}(u,v), \tag{55}$$

where

$$\sigma_u^2=\left(\frac{\partial u}{\partial x}\right)^2\sigma_x^2+\left(\frac{\partial u}{\partial y}\right)^2\sigma_y^2, \tag{56}$$

$$\sigma_v^2=\left(\frac{\partial v}{\partial x}\right)^2\sigma_x^2+\left(\frac{\partial v}{\partial y}\right)^2\sigma_y^2, \tag{57}$$

and

$$\operatorname{cov}(u,v)=\left(\frac{\partial u}{\partial x}\right)\left(\frac{\partial v}{\partial x}\right)\sigma_x^2+\left(\frac{\partial u}{\partial y}\right)\left(\frac{\partial v}{\partial y}\right)\sigma_y^2. \tag{58}$$

In some textbooks it is implicitly assumed that quantities such as u and v are statistically independent so that their covariance is zero and equations such as (56) and (57) with no covariance terms are given instead of the complete eq (55). The use of the complete equation is important in the present case; the extension of these equations from two to three variables is obvious.

Application of eqs (56) through (58) gives

$$\sigma_u^2=\sigma_{x1}^2+\sigma_{x2}^2+\sigma_{x3}^2, \tag{59}$$

$$\sigma_v^2=(x_2+x_3)^2\sigma_{x1}^2+(x_1+x_3)^2\sigma_{x2}^2+(x_1+x_2)^2\sigma_{x3}^2, \tag{60}$$

$$\sigma_w^2=(x_2x_3)^2\sigma_{x1}^2+(x_1x_3)^2\sigma_{x2}^2+(x_1x_2)^2\sigma_{x3}^2, \tag{61}$$

$$\operatorname{Cov}(u,v)=(x_2+x_3)\sigma_{x1}^2+(x_1+x_3)\sigma_{x2}^2+(x_1+x_2)\sigma_{x3}^2, \tag{62}$$

$$\operatorname{Cov}(u,w)=x_2x_3\sigma_{x1}^2+x_1x_3\sigma_{x2}^2+x_1x_2\sigma_{x3}^2, \tag{63}$$

and

$$\mathrm{Cov}\ (v,\ w)=(x_2+x_3)x_2x_3\sigma_{x1}^2+(x_1+x_3)x_1x_3\sigma_{x2}^2+(x_1+x_2)x_1x_2\sigma_{x3}^2, \tag{64}$$

where

$$\sigma_{x1}=2\rho v_1\sigma_1,\ \sigma_{x2}=2\rho v_2\sigma_2,\ \sigma_{x3}=2\rho v_3\sigma_3.$$

To use eq (55) for the standard deviations of the elastic constants one must compute the partial derivatives of these constants with respect to u, v, w. These partials of c_{11} can be obtained by taking derivatives of eq (45). The resulting expressions involve partials of the coefficients a_i and these in turn involve partials of the quantities defined in eqs (38) through (41). Let subscripts u, v, w denote partial differentiation with respect to u, v, w respectively. Then from eqs (38) through (41)

$$h_{1u}=(gk+jf)/e-h, \tag{65}$$

$$j_{1u}=2u[(jk+qf)/e-p], \tag{66}$$

$$k_{1u}=k(3u^2q-4v)/e-3u^2s, \tag{67}$$

$$p_{1u}=2uq, \tag{68}$$

$$j_{1v}=-4f/e, \tag{69}$$

$$k_{1v}=-4uk/e, \tag{70}$$

$$p_{1v}=-4 \tag{71}$$

$$k_{1w}=8 \tag{72}$$

and the following are all zero: h_{1v}, h_{1w}, j_{1w}, and p_{1w}. We shall next require the partial derivatives of the a_i which are given by differentiating eqs (46) through (52) with the result for the u derivatives

$$a_{0u}=3r^2p_1^2p_{1u}/e^3-2k_1k_{1u}, \tag{73}$$

$$a_{1u}=3r^2(jp_1^2+2ujp_1p_{1u})/e^3-2j_1k_{1u}-2k_1j_{1u}, \tag{74}$$

$$a_{2u}=3r^2(2gp_1p_{1u}+2uj^2p_1+u^2j^2p_{1u})/e^3-2h_1k_{1u}-2k_1h_{1u}-2j_1j_{1u}, \tag{75}$$

$$a_{3u}=r^2(6gjp_1+6ugjp_{1u}+3u^2j^3)/e^3-2(g_1k_{1u}+h_1j_{1u}+j_1h_{1u}), \tag{76}$$

$$a_{4u}=3r^2(2ugj^2+g^2p_{1u})/e^3-2g_1j_{1u}-2h_1h_{1u}, \tag{77}$$

$$a_{5u}=3r^2g^2j/e^3-2g_1h_{1u}, \tag{78}$$

and with a_{6u} equal to zero. For the v derivatives the result is

$$a_{0v}=-12r^2p_1^2/e^3-2k_1k_{1v}, \tag{79}$$

$$a_{1v}=-24r^2ujp_1/e^3-2j_1k_{1v}-2k_1j_{1v}, \tag{80}$$

$$a_{2v}=-12r^2(2gp_1+u^2j^2)/e^3-2h_1k_{1v}-2j_1j_{1v}, \tag{81}$$

$$a_{3v}=-24r^2ugj/e^3-2(g_1k_{1v}+h_1j_{1v}), \tag{82}$$

$$a_{4v}=-12r^2g^2/e^3-2g_1j_{1v}, \tag{83}$$

and with a_{5v} and a_{6v} equal to zero. For the w derivatives the result is

$$a_{0w}=-16k_1, \tag{84}$$

$$a_{1w}=-16j_1, \tag{85}$$

$$a_{2w}=-16h_1, \tag{86}$$

$$a_{3w}=-16g_1, \tag{87}$$

and with a_{4w}, a_{5w}, and a_{6w} equal to zero. Define

$$D=6a_6c_{11}^5+5a_5c_{11}^4+4a_4c_{11}^3+3a_3c_{11}^2+2a_2c_{11}+a_1 \tag{88}$$

then differentiation of eq (45) gives

$$c_{11u}=-(a_{5u}c_{11}^5+a_{4u}c_{11}^4+a_{3u}c_{11}^3+a_{2u}c_{11}^2+a_{1u}c_{11}+a_{0u})/D, \tag{89}$$

$$c_{11v}=-(a_{4v}c_{11}^4+a_{3v}c_{11}^3+a_{2v}c_{11}^2+a_{1v}c_{11}+a_{0v})/D, \tag{90}$$

and

$$c_{11w}=-(a_{3w}c_{11}^3+a_{2w}c_{11}^2+a_{1w}c_{11}+a_{0w})/D, \tag{91}$$

where we have assumed $D\neq 0$. For the [110] direction $D=0$ and a different treatment, described below, is required. The derivatives of c_{44} are obtained from (53) and are

$$c_{44u}=(1-c_{11u})/2, \tag{92}$$

$$c_{44\,v}=-c_{11\,v}/2, \tag{93}$$

and

$$c_{44w}=-c_{11w}/2. \tag{94}$$

The derivatives of c_{12} are obtained from eq (54) and so involve derivatives of γ. From (42) we have

$$\gamma^2=(gc_{11}^2+ujc_{11}+p_1)4e, \tag{95}$$

so that

$$(\gamma^2)_u=(2c_{11}gc_{11u}+jc_{11}+ujc_{11u}+p_{1u})/4e, \tag{96}$$

$$(\gamma^2)_v=(2c_{11}gc_{11v}+ujc_{11v}-4)/4e, \tag{97}$$

and

$$(\gamma^2)_w=(2c_{11}g+uj)c_{11w}/4e. \tag{98}$$

Now use $\gamma_u=(\gamma^2)_u/2\gamma$ and eq (54) to obtain

$$c_{12u}=(\gamma^2)_u/2\gamma-c_{44u}, \tag{99}$$

$$c_{12v}=(\gamma^2)_v/2\gamma-c_{44v}, \tag{100}$$

and

$$c_{12w}=(\gamma^2)_w/2\gamma-c_{44w}. \tag{101}$$

The expression for σ_{11}^2 is then

$$\sigma_{11}^2=c_{11u}^2\sigma_u^2+c_{11v}^2\sigma_v^2+c_{11w}^2\sigma_w^2+2c_{11u}c_{11v}\,\mathrm{cov}\,(u,v)+2c_{11u}c_{11w}\,\mathrm{cov}\,(u,w)+2c_{11v}c_{11w}\,\mathrm{cov}\,(v,w). \tag{102}$$

The equations for σ_{44}^2 and σ_{12}^2 are the same with the subscripts on c_{11} changed to 44 and 12 respectively.

The procedure for obtaining the desired standard deviations is thus straightforward although tedious. One begins by calculating the variances and covariances of u, v, w from eqs (59) through (64). Then compute in succession the quantities given by eqs (65) through (102).

Following eq (91) we noted that $D=0$ for the [110] direction. This can be seen as follows: For the [110] direction r is zero by eq (34) and the γ^3 term drops out of eq (43). Then eq (45) simply consists of the square of all the terms in (43) except $r\gamma^3$. Let

$$B=\alpha^3s_1/8+\alpha^2uh/8+\alpha u^2p/8+u^3s/8-\gamma^2(\alpha f+uk)/2-w. \tag{103}$$

Then eq (45) for the [110] direction is $B^2=0$, and D is then $D=2B\,\dfrac{dB}{d\alpha}$, and therefore $D=0$.

The foregoing statistical treatment thus fails for any direction for which c_{11} is a double root of eq (45). This appears to be true only for the [110] direction (we have already noted that the [100] and [111] directions are not suitable for the method of this paper) but the writers have not been able to construct a proof.

For the [110] direction the following results are well known and easily obtained from the treatment of Kolsky [9], for example. If x_1 corresponds to the longitudinal wave, x_2 to the transverse wave with displacement parallel to [001], and x_3 to the transverse wave with displacement parallel to [110], then

$$c_{11}=x_1-x_2+x_3, \tag{104}$$

$$c_{12}=x_1-x_2-x_3, \tag{105}$$

and

$$c_{44}=x_2. \tag{106}$$

These give

$$\sigma_{11}^2=\sigma_{12}^2=\sigma_{x1}^2+\sigma_{x2}^2+\sigma_{x3}^2, \tag{107}$$

and

$$\sigma_{44}=\sigma_{x2}. \tag{108}$$

We have assumed throughout this paper that errors in thickness and density can be neglected in comparison with errors in transit time t. If standard deviations were assigned to the thickness and density as well, the quantities x_i would not be statistically independent and two modifications of the foregoing treatment would be required. First, eqs (56) through (58) would have to be used with the thickness, density, and transit times as independent variables to give the variances and covariances of u, v, w. The calculations using eqs (65) through (102) would then go as before. Second, eqs (107) and (108) would have to be replaced by appropriate expressions in terms of the standard deviations of the thickness, density, and transit times derived from (56) through (58) and (104) through (106). No attempt has been made to allow for uncertainties in the orientation; such allowance should probably be made but appears to be an exceedingly difficult problem.

4. Procedure for Computing the Elastic Compliances and Their Standard Deviations

The foregoing results form a complete unit, giving the elastic constants, c_{ij}, and their standard deviations. The present section may be skipped unless it is desired to put the results in terms of the elastic compliances, s_{ij}. The calculation of the s_{ij} from the c_{ij} is trivial but the calculation of the standard deviations of the s_{ij} is more difficult and serious errors can result if the covariance terms are not taken into account. There appears to be no discussion of this problem in the literature on elastic constants, so we present the method for the cubic case.

The well-known equations for the elastic compliances of a cubic crystal in terms of the elastic constants are

$$s_{11}=(c_{11}+c_{12})/c, \tag{109}$$

$$s_{12}=-c_{12}/c, \tag{110}$$

and

$$s_{44,}=1/c_{44,} \tag{111}$$

where

$$c=(c_{11}-c_{12})(c_{11}+2c_{12}). \tag{112}$$

To compute the standard deviations of the s_{ij} one can apply eq (55) which requires the covariances of the c_{ij}. To compute these covariances one might try to use eq (58) which would be wrong because x and y were assumed to be statistically independent. We require the more general formula

$$\operatorname{cov}(F,G)=\frac{\partial F}{\partial u}\frac{\partial G}{\partial u}\sigma_u^2+\frac{\partial F}{\partial v}\frac{\partial G}{\partial v}\sigma_v^2+\left(\frac{\partial F}{\partial u}\frac{\partial G}{\partial v}+\frac{\partial F}{\partial v}\frac{\partial G}{\partial u}\right)\operatorname{cov}(u,v) \tag{113}$$

for the covariance [12] of F and G which are defined in terms of quantities u and v which are not statistically independent. Writing cov (11, 12) for the covariance of c_{11} and c_{12} we have

$$\mathrm{cov}\ (11,\ 12)=c_{11u}c_{12u}\sigma_u^2+c_{11v}c_{12v}\sigma_v^2+c_{11w}c_{12w}\sigma_w^2+(c_{11u}c_{12v}+c_{11v}c_{12u})\ \mathrm{cov}\ (u,\ v)$$
$$+(c_{11u}c_{12w}+c_{11w}c_{12u})\ \mathrm{cov}\ (u,\ w)+(c_{11v}c_{12w}+c_{11w}c_{12v})\ \mathrm{cov}\ (v,\ w) \tag{114}$$

The expressions for cov (11, 44) and cov (12, 44) are identical except for the appropriate changes of subscripts, but we shall not need to calculate these latter two covariances. Writing $s_{11,\,11}$ for $\frac{\partial s_{11}}{\partial c_{11}}$ and similarly for other partials we have

$$s_{11,\,11}=c-\frac{(c_{11}+c_{12})(2c_{11}+c_{12})}{c^2}, \tag{115}$$

$$s_{11,\,12}=c+\frac{(c_{11}+c_{12})(4c_{12}+c_{11})}{c^2}, \tag{116}$$

$$s_{12,\,11}=\frac{c_{12}(2c_{11}+c_{12})}{c^2}, \tag{117}$$

$$s_{12,\,12}=-\frac{(c_{11}+c_{12})(4c_{12}-c_{11})}{c^2}, \tag{118}$$

$$s_{44,\,44}=-1/c_{44}^2, \tag{119}$$

and with $s_{11,\,44}$, $s_{12,\,44}$, $s_{44,\,11}$, $s_{44,\,12}$ all zero. Letting σs_{11} represent the standard deviation of s_{11} and similarly for the other s_{ij},

we have

$$\sigma_{s_{11}}^2=s_{11,\,11}^2\sigma_{11}^2+s_{11,\,12}^2\sigma_{12}^2+2s_{11,\,11}s_{11,\,12}\ \mathrm{cov}\ (11,\ 12) \tag{120}$$

$$\sigma_{s_{12}}^2=s_{12,\,11}^2\sigma_{11}^2+s_{12,\,12}^2\sigma_{12}^2+2s_{12,\,11}s_{12,\,12}\ \mathrm{cov}\ (11,\ 12), \tag{121}$$

and

$$\sigma_{s_{44}}=\sigma_{44}/c_{44}^2. \tag{122}$$

For the [110] direction the covariances of c_{11} and c_{12} is best calculated directly from (104) and (105) using (58). The result is

$$\mathrm{cov}\ (11,\ 12)=\sigma_{x1}^2+\sigma_{x2}^2+\sigma_{x3}^2. \tag{123}$$

Thus, the procedure for calculating the standard deviation of the s_{ij} for any direction, including the [100] and [111], is to use eqs (120) through (122) evaluating the partial derivations from eqs (115) through (119). The situation considered in the present paper, using only information obtainable from measurements in a single direction, compels us to exclude [100] and [111] from the present considerations. For [110] cov (11, 12) is given by (123); for any other direction, it is given by (114).

5. Measurements on $SrTiO_3$

The writers carried out a series of measurements on a boule of strontium titanate, kindly supplied by the National Lead Company, to check the method. The density value [*13*] of 5.116 g/cm^3 was used. Flats were first ground to give the maximum thickness between parallel faces permitted by the shape of the crystal. A series of measurements was taken and analyzed. The crystal was then recut normal to the [110] direction and a second series of measurements was then made. The measurements were all made with 10 Mc/s X-cut and AC-cut quartz crystals 0.25 in. in diameter. A commercial pulsed oscillator was used to drive these transducers. The echoes were observed on a dual trace oscilloscope simultaneously with a 1 Mc/s standard frequency signal. The results are sumarized in table 1.

Table 1. *Data on* $SrTiO_3$ *at 25° C*

Parameter	Symbol	First direction	Second direction, [110]
Direction	l	0.67905	0.70711
Cosines	m	.27160	.70711
	n	.68200	.00000
Length, cm		5.3045	4.5670
Transit times, 10^{-6} sec	t_1	13.15±0.10	11.36±0.05
	t_2	22.08±.05	18.71±.07
	t_3	23.15±.07	20.02±.09
x_i, 10^{12} dyne/cm^2	x_1	3.330±.051	3.308±.029
	x_2	1.181±.005	1.219±.009
	x_3	1.074±.006	1.064±.010

6. Results

The data are summarized in table 1. The calculation of c_{11} by the method of eqs (20) through (52) was programmed for an automatic computer using an iterative procedure of solving eq (45) which gives the real roots to four places in the interval 0.0 to 5.0×10^{12} dynes/cm^2. For the first direction, there is a single root at $\alpha=3.162$ and a single root at $\alpha=3.497\times10^{12}$ dynes/cm^2. For the second direction there is a double root at $\alpha=3.153$ and a double root at $\alpha=3.462\times10^{12}$ dynes/cm^2. A complete set of elastic constants was computed for each of these possible choices of c_{11} and the results are compared in table 2. The choice of 3.497 and 3.462 leads to a disagreement in c_{12} which is outside the experimental error. The choice of 3.162 and 3.153 gives consistent sets of constants. The latter choice is also known to be correct because 3.153 is obtained from eq (104) when x_2 and x_3 are properly distinguished by the polarization of the corresponding sound waves.

For the first direction, the standard deviations of the c_{ij} were determined by the method of eqs (59) through (102) using an automatic computer. Equations (107) and (108) were used for the second direction. The final values for the c_{ij} were computed by averaging the results for the two directions weighted by the reciprocals of the squares of the standard deviations. The s_{ij} values were then computed from eqs (109) through (112) and their standard deviations from eqs (113) through (123).

Table 2. *Comparison of possible sets of elastic constants*

Constants	First direction	Second direction
Computed from correct choice of root for c_{11}		
c_{11}	3.162±0.052	3.153±0.032
c_{12}	1.035± .052	1.024± .032
c_{44}	1.212± .007	1.219± .009
Computed from incorrect choice of root for c_{11}		
c_{11}	3.497	3.462±0.032
c_{12}	1.200	1.024± .032
c_{44}	1.044	1.064± .010

The c_{11} and c_{12} values of Bell and Rupprecht [*14*] agree within experimental error with the results of the present work as shown in table 3; the c_{12} value of Poindexter and Giardini [*15*] also agrees within experimental error, but their c_{11} value differs from the present result by much more than twice the standard deviation and so is significantly different from our result. The other workers' c_{44} values lie on either side by slightly more than twice the standard deviation of our value, but are probably within the combined experimental error of their determination and ours. The writers feel that the c_{11} values of Poindexter and Giardini should be rejected and that the remaining data show reasonable agreement.

The anisotropy of a cubic crystal depends on the quantity δ defined by

$$\delta=2s_{11}-2s_{12}-s_{44}. \tag{124}$$

The Young's modulus, Y_f, and shear modulus, G_f, are given as a function of the usual spherical polar angles by

$$\frac{1}{Y_f}=s_{11}-\delta \sin^2 \theta \cos^2 \theta-(\delta/4) \sin^4 \theta \sin^2 2\phi, \tag{125}$$

and

$$\frac{1}{G_f}=s_{44}+2\delta \sin^2 \theta \cos^2 \theta+(\delta/2) \sin^4 \theta \sin^2 2\phi. \tag{126}$$

These quantities are plotted in figure 1 which shows that $SrTiO_3$ comes close to being isotropic; Young's modulus varies by only 10 percent and the shear modulus by 5 percent.

TABLE 3. *Comparison with elastic constants of $SrTiO_3$ at 25°C determined by other workers*

Constants	Poindexter and Giardini [a]	Bell and Rupprecht [b]	Present work [b]	Percent difference, last two columns
c_{11}	3.48	3.181	3.156±0.027	0.79
c_{12}	1.01	1.025	1.027± .027	0.19
c_{44}	1.19	1.236	1.215± .006	1.73
s_{11}	3.3	3.729	3.772± .023	1.14
s_{12}	−0.74	−0.909	−0.926± .010	1.84
s_{44}	8.4	8.091	8.233± .040	1.73

All c_{ij} in units of 10^{12} dyne/cm_2; s_{ij} in units of $10-^{13}$ cm^2/dyne.

[a] s_{ij} determined by resonance method and c_{ij} by matrix inversion.

[b] c_{ij} determined by pulse velocity method and s_{ij} by matrix inversion.

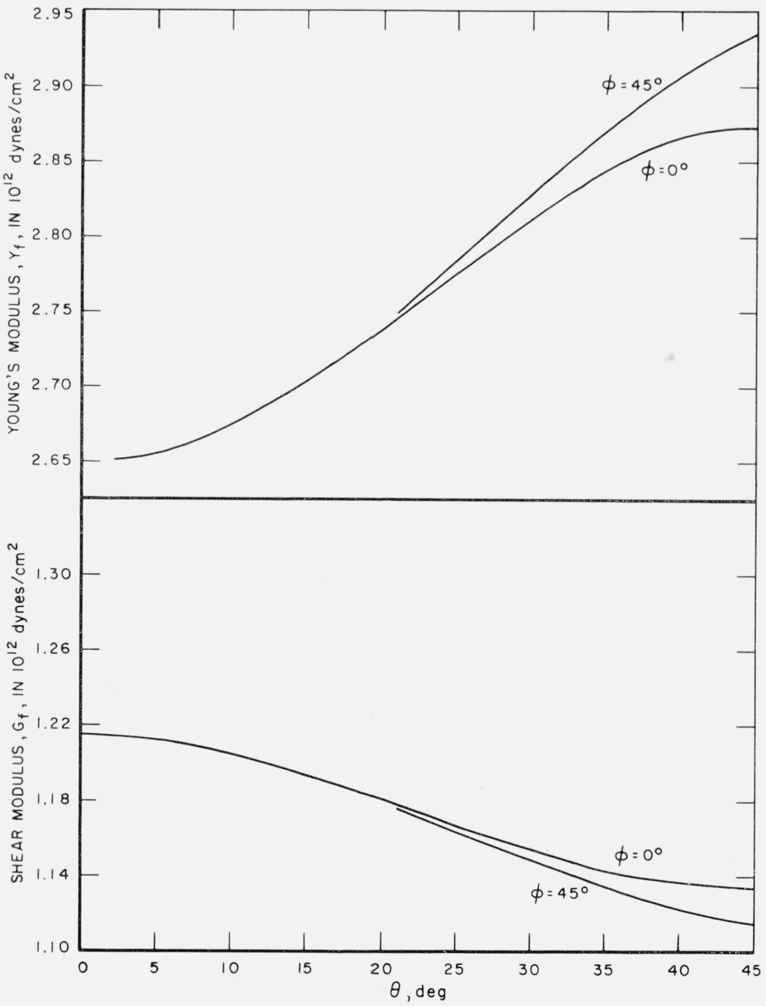

FIGURE 1. *Young's modulus, Y_f, and the shear modulus, G_f, as a function of orientation.*

The colatitude, θ, is the angle between the [001] direction and the direction of measurement. The azimuth, ϕ, is the angle between the [100] direction and the projection of the direction of measurement on the (001) plane. The subscript f indicates that the elastic moduli are for a free specimen which is under no constraint.

7. Summary

(1) Velocity measurements in a single direction in a cubic crystal provide enough information to determine the three elastic constants, c_{ij}, except for the [100] and [111] directions which are therefore excluded from consideration in this paper.

(2) For the [110] direction the computation of the elastic constants and their standard deviations is simple and is given in eqs (104) through (108).

(3) For all other directions the calculations are much more complex. The general procedure for the elastic constants (applicable also to the [110] direction) is given in eqs (2) through (54). The general procedure for the standard deviations (not applicable to the [110] direction) is given in eqs (59) through (102).

(4) The procedure for calculating the elastic compliances, s_{ij}, and their standard deviations is given in eqs (109) through (123). Throughout the statistical treatment the covariance terms are included and their importance is emphasized.

(5) The method is applied to $SrTiO_3$ and results in good agreement with previous workers are obtained.

The writers thank W. E. Tefft of the National Bureau of Standards for bringing eqs (55) and (58) to their attention, and M. D. Beals of the National Lead Company for supplying the $SrTiO_3$ specimen.

8. References

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(Paper 67A2–205)

JOURNAL OF RESEARCH of the National Bureau of Standards—A. Physics and Chemistry
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Publications of the National Bureau of Standards*

Selected Abstracts

A new type of computable inductor, C. H. Page, *J. Research NBS* **67B** *(Math. and Math. Phys.), No. 1 (Jan.-Mar. 1963), 75 cents.*
The mutual inductance analog of the generalized Thompson-Lamparo theorem (for cross-capacitances) is developed. An infinitely long cage of five parallel wires can yield an absolute inductance of

$$10^{-7} \ln \frac{3+\sqrt{5}}{2}$$

henries per meter. End-effects of order $1/l^2$ occur in a finite cage, but can be reduced to order $1/l^4$ by using eight wires.
The eight wire cage has the advantage of overdetermined relations among the inductances to be measured, allowing an estimate of experimental error in the calibration of a standard. Errors due to faulty cage geometry are shown to be of the order of 1 in 10^7.

Numerical computation of the temporal development of currents in a gas discharge tube, W. Börsch-Supan and H. Oser, *J. Research NBS* **67B** *(Math. and Math. Phys.), No. 1 (Jan.-Mar. 1963), 75 cents*
The behavior of electrical currents in a gas discharge tube including space charge effects is investigated by numerical integration of the governing nonlinear partial differential equations. Both stationary solutions and the temporal development, under the influence of space charge effects, are considered. The numerical integration is done by a difference method. It is found that the truncation error can be greatly reduced by comparison with formal solutions for constant fields. The discussion is essentially restricted to the more mathematical questions.

Equipment for single crystal growth from aqueous solution, J. L. Torgesen, A. T. Horton, and C. P. Saylor, *J. Research NBS* **67C** *(Eng. and Instr.), No. 1 (Jan.-Mar. 1963), 75 cents.*
The growing of large single crystals of high quality from solution requires the precise control of supersaturation and the avoidance of thermal amd mechanical shock. Uniform growth conditions and cleanliness need to be maintained. Good seed crystals are necessary and the accidental introduction or generation of new nuclei should be prevented insofar as possible. In the apparatus and equipment assemblies here described, the crystal-growth bath is designed for uniform growth conditions and the exclusion of contamination. The support for the crystals provides for convenient mounting of the seeds, holds the crystals firmly, and allows their easy removal with minimum damage. A new reversing rotation mechanism promotes equal washing of the crystal surfaces and achieves uniform temperature and composition of the solution without, at the same time, producing significant mechanical stresses in the crystals. The temperature controller gives regulation of the temperature an order of magnitude more sensitive than those hitherto used and provides for stepless change of temperature. The crystals are thus free from liquid inclusions found to result from sudden acceleration of growth. The electrolytic conductance of ionic solutions may be used as a precise and sensitive measure of solution concentration and supersaturation. The crystal-growth procedures which are reported have resulted in the production of very good single crystals of a considerable variety of chemical phases.

An automatic multichannel correlator, R. F. Brown, Jr., *J. Research NBS* **67C** *(Eng. and Instr.), No. 1 (Jan.-Mar. 1963), 75 cents.*
Very early in our Infrasonic Research Program it become apparent that the only way to differentitate between local meteorological pressure variations and the infrasonic signals from distant sources was through the relative time of arrival of the pressure disturbance at pickups spaced several miles apart. The "Multichannel Correlator" is an analog computer that was designed to detect these infrasonic signals.
At each pickup the pressure variations are converted to FM audio signals which are transmitted over leased telephone lines to the correlator. At the correlator these FM signals are demodulated and recorded on a ¼ inch per minute multichannel magnetic tape. The recorded data frequency range is 0.02 to 1.0 c/s and the pressure range is 0.1 to 50 dynes per square centimeter. 10 minute blocks of data are read from the tape and amplitude equalized to a constant rms value. A programmed time delay device produces the equivalent delays appropriate to a continuous horizontal azimuth search for velocities in the range of 280 to 400 meters per second. The correlator output is a continuous record of the average of the rectified sum of the delayed channel signals.

Elastic constant—porosity relations for polycrystalline thoria, S. Spinner, F. P. Knudsen, and L. Stone, *J. Research NBS* **67C** *(Eng. and Instr.), No. 1 (Jan.-Mar. 1963), 75 cents.*
The relations between the elastic constants and porosity for about 300 thoria specimens have been determined. Both Young's and the shear modulus for each specimen were obtained by a dynamic resonance method. From these two moduli, Poisson's ratio was computed. The tendency for all these elastic constants to decrease with increasing porosity is in qualitative agreement with theory. However, the decrease in the experimental values was greater than would be expected from the theory. This greater decrease for the experimental values is attributed to the fact that the specimens do not conform to the idealized assumptions of the theory.

New fast-opening, large-aperture shutter for high-speed photography, E. C. Cassidy and D. H. Tsai, *J. Research NBS* **67C** *(Eng. and Instr.), No. 1 (Jan.-Mar. 1963), 75 cents.*
This shutter consists essentially of a metallic foil in a capacitor discharge circuit. The opening action is obtained when the foil is compressed by the electromagnetic forces which accompany the heavy surge current through the circuit, during a transient discharge. A shutter made up of two foils in a loop arrangement may be opened to an area 1 in. x 3 in. in less than 45 μsec. The factors affecting the design and operation of this shutter are analyzed. These factors include the circuit parameters, the energy input to the foil, and the materials and the size of the foil. Some experimental results are also given.

Perturbation method in a problem of waveguide theory, D. Fox and W. Magnus, *J. Research NBS* **67D** *(Radio Prop.), No. 2 (Mar.-Apr. 1963), 70 cents.*
The reflection coefficient for the basic mode in a widening, straight, two-dimensional waveguide is computed for small wave numbers by using the perturbation method with the electrostatic case as the unperturbed case. The problem is treated as a perturbed infinite system of inhomogeneous linear equations, and it is shown that the matrix of the unperturbed system (which corresponds to the electrostatic case) can be inverted explicitly by using conformal mappings and physically unrealistic modes. Questions of convergence are discussed, and other examples for application of the method are indicated.

Some wave functions and potential functions pertaining to spherically stratified media, C. T. Tai, *J. Research NBS* **67D** *(Radio Prop.), No. 2 (Mar.-Apr. 1963), 70 cents.*
The wave functions pertaining to a bilinearly stratified medium are presented in this paper. Solutions to the equation $\nabla \cdot [\kappa(r)\nabla\psi]=0$ have been investigated for several profiles of $\kappa(r)$. An analysis is given to the equation

$\nabla \cdot [\overleftrightarrow{\kappa} \cdot \nabla\psi] = -\rho/\epsilon_0$ which arises from the formulation of the quasi-static electric field in a homogeneous anisotropic medium.

Radiation from a plasma-clad axially-slotted cylinder, W. V. T. Rusch, *J. Research NBS* **67D** (*Radio Prop.*), *No. 2* (*Mar.–Apr. 1963*), *70 cents.*
Expressions have been developed for the complete radiation pattern from a finite axial slot on an infinite circular cylinder covered with a homogeneous, uniform plasma sheath. The resulting field expressions are functions of both the longitude angle, ϕ, and the polar angle, θ. Numerical results have been obtained for a thin lossless plasma to determine the variation of the field pattern with plasma frequency, plasma thickness, slot width, and cylinder radius. These results are presented graphically to illustrate various properties of the radiating system.

Report of the 47th National Conference on Weights and Measures, 1962, *NBS Misc. Publ. 244* (*November 23, 1962*), *75 cents.*
A report of the proceedings of the forty-seventh National Conference on Weights and Measures, held in Washington, D.C., June 4, 5, 6, 7, and 8, 1962, and attended by State, county, and city weights and measures officials. 167 p.

Radiation quantities and units, International Commission on Radiological Units and Measurements (ICRU) Report 10a, 1962, *NBS Handb. 84* (*Nov. 14, 1962*), *20 cents.*
This Handbook presents definitions of twenty-three fundamental radiation quantities and units. It resulted from a three-year study by the *Ad Hoc* Committee on Quantities and Units of the ICRU. It includes new names for certain quantities and clarified definitions for others. It presents a system of concepts and a set of definitions which is internally consistent and yet of sufficient generality to cover present requirements and such future requirements as can be foreseen.

Controlled temperature oil baths for saturated standard cells, P. H. Lowrie, Jr., *NBS Tech. Note 141* (*August 1962*), *25 cents.*
Two oil baths for the temperature control of saturated standard cells have been designed and fabricated at the Boulder Laboratories of the National Bureau of Standards for operation at 28° C and 35° C respectively. Short term control to better than ±0.001° C with day-to-day variations no greater than 0.002° C has been achieved with the use of a mercury-toluene thermoregulator incorporating a temperature anticipating device. The circulating system limits temperature gradients in the oil to less than 0.001° C across any 10 inch section. The baths incorporate pre-heat and drain tanks as well as the main temperature regulated tank to facilitate the insertion and removal of cells and to minimize oil spillage.

Applications of resistance thermometers to calorimetry, G. T. Furukawa, *Book, Temperature, Its Measurement and Control in Science and Industry III, pt. 2, 317–328* (*1962*).
The importance of the resistance thermometer in the accurate measurement of both temperature and the heat leak of the calorimeter is discussed. The final accuracy of the determination of heat capacity is shown to be dependent upon the accurate and consistent measurement of heat input to the sample and the corresponding rise in temperature. The various heat-capacity calorimeters used in the range from 10 to 400 °K are briefly described with emphasis upon the applications of resistance thermometers, the methods for calibrating them, and the problems associated with the design of calorimeter vessels. Comparison is made of the thermometric properties of platinum, copper, indium, lead and gold-silver alloy. The need for high relative accuracy in the measurement of $\triangle$R is emphasized. The various temperature scales used in calorimetry are compared and their applications are described.

Absorption spectrum of carbon vapor in solid argon at 4° and 20°K, R. L. Barger and H. P. Broida, *J. Chem. Phys.* **37,** *No. 5, 1152–1153* (*Sept. 1, 1962*).
Absorption spectra have been observed photoelectrically for C_3 and C_2 in solid argon at temperatures of 4° K and 20° K. A molecular beam of carbon from a Knudsen cell at 2550° K was deposited simultaneously with argon onto a quartz surface, cooled either with liquid helium or with liquid hydrogen. The spectra consist of 21 lines and a continuum between 3797A and 4221A attributed to C_3, and two lines at 5208A and 5269A attributed to C_2. Measured wavelengths, half-widths, peak absorption intensities and *f*-values are given. An *f*-value of 2×10^{-4} was found for the 5269A line of the C_2 and the 4102A line of C_3.

Vibrational-rotational spectroscopy, H. C. Allen, Jr. and W. B. Olson, *Ann. Rev. Phys. Chem.* **13,** *221–240* (*1962*).
The literature on molecular spectroscopy has increased significantly each year with the increased availability of high-quality commercial infrared spectrometers. This year is no exception. It is quite impossible to give a complete review of all the work in the space available, hence the authors will take advantage of their prerogative of discussing a limited number of topics. We shall, thus, stress work of a general nature on theoretical advances, fine structure of simple molecules, vibrational spectra, intensities of gases, and computer applications. For the spectra of specific molecules the reader is referred to *Chemical Abstracts.*

Realistic diatomic potential function, H. W. Woolley, *J. Chem. Phys.* **37,** *No. 6, 1307–1316* (*Sept. 1962*).
An examination of recently published data for diatomic molecules as obtained by the Rydberg-Klein-Rees method has suggested a useful form for the potential energy function. This term provides an inverse power dependence at large distance and an extrapolation to infinity at the extreme of close approach. A three parameter potential obtained by fitting in lowest approximation is compared with empirical data on $\omega_e X_e$ and α_e. Relations are also given to permit an arbitrarily close fit of observed spectroscopic constants. Theoretical formulas covering seven new Y_{ij}'s of the Dunham-Sandeman series for the rotating-vibrator are included. Potential curves for H_2 and HF are shown as examples, including effects of previously determined higher order spectroscopic constants. Other applications of the new potential are also discussed.

Optical constants of aluminum in vacuum ultraviolet, R. LaVilla and H. Mendlowitz, *Phys. Rev. Letters* **9,** *No. 4, 149–150* (*Aug. 15, 1962*).
Values of the frequency dependent complex dielectric constant $\epsilon(\omega)$ of aluminum in the photon energy region of 12–16 ev were derived from the characteristic electron energy loss spectra. A two-parameter Drude model with N, the number of "free" electrons per atom, as 2.6 and τ, the relaxation time as 1.1×10^{-15} sec. was found to give a good approximation to the optical properties of aluminum.

Microwave spectrum of methyldifluoroarsine, L. J. Nugent and C. D. Cornwell, *J. Chem. Phys.* **37,** *No. 3, 523–534* (*Aug. 1962*).
The spectrum of CH_3AsF_2 was investigated over the range 10–33 KMc/sec. Three Q-branches ($K=5-4$, $6-5$, $7-6$) and two *R* transitions ($J=2-3$, $K=2-3$; $J=3-4$, $K=3-4$) were fitted by a Hamiltonian which included terms for overall rotation, internal rotation, nuclear quadrupole coupling, and centrifugal distortion. The reciprocal moments of inertia are $A=5414.49\pm0.04$ Mc/sec, $B=5381.28\pm0.03$ Mc/sec, and $C=3871.88\pm0.03$ Mc/sec. The *b*-axis is perpendicular to the plane of symmetry. The height of the internal rotation barrier (assumed to be sinusoidal) is 466 ± 10 cm^{-1}. With the bond length $r_{\mathrm{CH}}=1.095$ A assumed, the spectral data yield $r_{\mathrm{AsC}}=1.930\pm0.010$ A, $r_{\mathrm{AsF}}=1.734\mp0.005$ A $\angle\mathrm{HCH}=109°9'\pm1°$, $\angle\mathrm{CAsF}=95°40'\pm14'$, $\angle\mathrm{FAsF}=96°18'\pm16'$. The quadrupole coupling constants for As^{75} are $eQq_{cc}=-220\pm4$ Mc/sec and $\eta_0=(q_{bb}-q_{\mathrm{aa}})/q_{cc}=-1.20\pm0.05$. The indicated uncertainties of all parameters are limits of error obtained directly from the estimated maximum imprecision in the measured frequencies.

New wavemeter for millimeter wavelengths, R. W. Zimmerer, *Rev. Sci. Instr.* **33,** *No. 8, 858–859* (*Aug. 1962*).
A new wavemeter of simple design is described. The principle of operation makes use of a new development in physical optics. The actual performance of the devise was measured and compared with the theory.

Electron energy losses in solids and their influence on the electron diffraction diagram, L. Marton, *J. Phys. Soc. Japan* **17,** *Suppl. B–II, 68–73 (1961).*
The electron diffraction diagram is considered from the point of view of the influence of characteristic energy losses of the electrons in the solid. Some of the present theories of these losses are reviewed, together with the experimental evidence, leading to a new viewpoint. While the influence of these characteristic losses on the average electron diffraction diagram is negligible, for precise measurements a knowledge of the losses and a corresponding correction (either theoretical or experimental) is needed.

Optical detection of microwave transitions in electronically excited CN produced by a chemical reaction, R. L. Barger, H. P. Broida, A. J. Estin, and H. E. Radford, *Phys. Rev. Letters* **9,** *No. 8, 345–346 (Oct. 15, 1962).*
Population inversions and non-equilibrium populations produced by chemical reactions should be useful for molecular structure studies by double resonance and possibly for maser or laser action. Atomic flames of nitrogen atoms mixed with hydrocarbons provide a particularly good example of a chemical reaction which produces population inversion. A TE_{011} microwave cavity of volume 40 cm^3, from 8750 to 10,200 Mc and having a Q of approximately 2×10^4, was used with a power input of ½ to 1 watt. At each of the frequencies 9855, 9740, and 8810 Mc, a resonant increase in the optical emission was observed; the increases had ralative magnitudes of 5, 4, and 1, respectively.

Sum rules for vibrational-rotational energy levels including centrifugal distortion, H. C. Allen, Jr., and W. B. Olson *J. ehem. Phys.* **37,** *No. 2, 212–214 (July 15, 1962).*
Sum rules are developed for the vibrational-rotational energy levels of an asymmetric rotor. These sum rules contain the corrections for centrifugal distortion correct for terms of the order P^4 in the Hamiltonian. If the P^4 terms of the Hamiltonian are neglected these sum rules reduce to those derived for a rigid asymmetric rotor by Mecke.

Rotational perturbations in CN I. Zero-field theory, optical Zeeman effect, and microwave transition probabilities, H. E. Radford and H. P. Broida, *Phys. Rev.* **128,** *No. 1, 231–242 (Oct. 1963).*
The theory of rotational perturbations in doublet states of diatomic molecules is developed and is applied to the long-standing problem of perturbations in the violet bands of the CN radical. Analysis of the available optical data yields experimental values of two reduced matrix elements:

$$(\Pi|AL_y|\Sigma) = -0.39 \pm 0.04 \text{ cm}^{-1}$$
$$(\Pi|BL_y|\Sigma) = 0.011 \pm 0.001 \text{ cm}^{-1},$$

where the uncertainties shown are estimated upper limits These account satisfactorily for all the observed line shifts in the violet spectrum. These two parameters are then used to predict the Zeeman effect of the rotational perturbations, and these predictions are checked against new observations of the CN violet specturm at magnetic field strengths up to 28 kgauss. Finally, the zero-field analysis is used to examine the feasibility of a proposed microwave resonance investigation of the perturbed excited states of CN.

The system of Bi_2O_3–B_2O_3, E. M. Levin and C. L. McDaniel. *J. Am. Ceram. Soc.* **45,** *No. 8, 355–360 (Aug. 1962).*
The phase diagram for the system Bi_2O_3–B_2O_3 has been determined experimentally. The melting point of Bi_2O_3 has been redetermined as 825° C with an estimated overall uncertainty of about ±3° C, and the molal heat of fusion of Bi_2O_3, calculated from the slope of the liquidus curve, is 2050 cal per mole. The system contains a body-centered cubic phase of approximate composition $12Bi_2O_3 \cdot B_2O_3$, which melts incongruently at 632° C. Four congurently melting compounds exist in the system: $2Bi_2O_3 \cdot B_2O_3$, $3Bi_2O_3 \cdot 5B_2O_3$, $Bi_2O_3 \cdot 3B_2O_3$, and $Bi_2O_3 \cdot 4B_2O_3$, with melting points, respectively, of 675°, 722°, 708°, and 715° C. The $Bi_2O_3 \cdot 4B_2O_3$ compound exhibits a sluggish transformation at 696° C. Compositions containing up to 97.5 wt% (85 mole %) Bi_2O_3 can be partly or totally quenched to glass. Indices of the quenched glasses are greater than 1.74. A region of liquid immiscibility extends at 709° C from almost pure B_2O_3 to 19.0 mole % Bi_2O_3. The extent of immiscibility theoretically calculated agrees with the experimentally determined value when 1.20 A is used for the ionic radius of Bi^{3+}.

Wavelengths, energy levels, and pressure shifts in mercury 198, V. Kaufman, *J. Opt. Soc. Am.* **52,** *No. 8, 866–870 (Aug. 1962).*
The vacuum wavelengths of 27 lines in the spectrum of Hg^{198} have been measured relative to the international standard of length, the Kr^{86} line at 6057.80211 Å by photographic Fabry-Perot interferometry. These measurements were made using Hg^{198} electrodeless lamps containing argon gas at pressures of ¼, 3 and 10 mm Hg. Energy level values have been derived for each of the Hg^{198} sources. On the basis of these values, the energy level shifts per unit pressure of argon have been calculated. The suitability of the Hg^{198} electrodeless lamp as a source of wavelength standards for interferometric measurement of length and wavelength is discussed.
The standard source used was a Kr^{86} hot cathode lamp operated according to the conditions proscribed by the International Conference on Weights and Measures in 1960.

A network transfer theorem, G. F. Montgomery, *IRE Trans. Audio.* **AU–10,** *No. 3, 88 (May–June 1962).*
For a linear, passive, reciprocal two-port network, the forward, open-circuit voltage transfer ratio is equal to the reverse, short-circuit current transfer ratio.

Acoustical interferometer employed as an instrument for measuring low absolute temperatures, *J. Acoust, Soc. Am.* **34,** *No. 8, 1145–1146 (Aug. 1962).*
Values of absolute temperatures at 2 and 20° K have been determined from experimental measurements of the speed of sound as a function of pressure in helium gas. The acoustical interferometer was the instrument employed in the measurements, and the accuracy achieved in the experiment indicates that sonic thermometry at low tempertures may be competitive with other conventional thermometry techniques.

Kinetics of Cs^+ desorption from tungsten, M. D. Scheer and J. Fine, *J. Chem. Phys.* **37,** *No. 1, 107–113 (July 1962).*
The mean absorption lifetime (τ_3) of Cs^+ on tungsten has been measured in the 1000–1200°K temperature range, using a pulsed beam technique. Under conditions of low surface coverage and with either Cs or CsI as beam materials,

$$\tau_3 = (1.0 \pm 0.5) \times 10^{-12} \exp\left[\frac{23{,}6000 \pm 500}{T}\right] \text{sec.}$$

was obtained. The heat of desorption can be calculated as the energy required to remove an isolated Cs^+ ion from the surface of an electrical conductor. The presence of an absorbed contaminating layer, arising from residual vacuum gases, decreased the Cs^+—W binding energy by 0.5 ev and increased the pre-exponential factor by about two orders of magnitude. Anomolous results were obtained when CsCl was used for a beam material, suggesting a reaction between the surface tungsten atoms and atomic chlorine.

Structure and structure imperfections of solid β-oxygen, E. M. Horl, *Acta, Cryst.* **15,** *No. 9, 845–850 (Sept. 1962).*
Electron diffraction studies were carried out on thin films of solid oxygen. The structure of β-oxygen was investigated and a rhombohedral structure of the space group $P3_121$ found. Its corresponding hexagonal cell has the dimensions $a = 3.307 \pm .008$Å, $c = 11.256 \pm .015$Å and contains three molecules parallel to the hexagonal axis at the positions: $(\frac{1}{3}, \frac{1}{3}, 0)$, $(-\frac{1}{3}, 0, \frac{1}{3})$ and $(0, -\frac{1}{3}, \frac{2}{3})$. Faults in the stacking sequence of the (00.1)-layers were observed and the experimental results compared with the Paterson treatment of growth faults in fcc crystals.

Neutral meson photoproduction from complex nuclei, R. A. Schrack, J. E. Leiss, and S. Penner, *Phys. Rev.* **127,** *No. 5, 1772–1783 (Sept. 1, 1962).*

The angular distributions of neutral mesons produced by 170 Mev bremsstrahlung on carbon, aluminum, copper, cadmium, and lead have been obtained through the coincident detection of the decay photons by a scintillation counter system. The experimental data have been analyzed by means of a Monte Carlo prediction based on an impulse-approximation elastic coherent production model. The nuclear density distributions which were used in the synthesis of those predictions which were in best agreement with the experimental data from this experiment have been compared to the charge density distributions inferred from electron scattering experiments. The values of the rms radii of nuclear matter obtained in this experiment are, within the limits of error of the experiment (about $2. \times 10^{-14}$cm), consistent with the values of charge distribution radii obtained in electron scattering.

The spin-independent part of the neutral meson photoproduction cross section used in the synthesized predictions is obtained using the dispersion theory of Chew, Low, Goldberger, and Nambu. The dependence of the cross section on the meson-nucleon phase shifts used is investigated and a set of phase shifts is presented that results in a correct prediction of the absolute cross sections observed in this experiment; however, this particular set of phase shifts is not unique.

Rotation-vibration spectrum of matrix-isolated hydrogen chloride, L. J. Schoen and D. E. Mann, *J. Chem. Phys.* **37,** *No. 5, 1146–1147 (Sept. 1, 1962).*

An infrared vibration-rotation spectrum of hydrogen chloride molecules isolated in solid argon matrices at 1:500 dilution has been observed at 4 and 20 °K in the region of the fundamental. From the contraction in spacing of the P(1) and R(0) it has been deduced that the HCl molecules undergo quantized but hindered rotation in cavities having cylindrical symmetry.

Other NBS Publications

Journal of Research 67B (Math. and Math. Phys.), No. 1 (Jan.–Mar. 1963) 75 cents.

Evaluation of a generalized elliptic-type integral. L. F. Epstein and J. H. Hubbell.

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A new type of computable inductor. C. H. Page. (See above abstract.)

Numerical computation of the temporal development of currents in a gas discharge tube. W. Börsch-Supan and H. Oser. (See above abstract.)

Tables of genera of groups of linear fractional transformations. H. Fell, M. Newman, and E. Ordman.

Journal of Research 67C (Eng. and Instr.), No. 1 (Jan.–Mar. 1963), 75 cents.

Method for calibrating a standard volt box. B. L. Dunfee.

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Equipment for single crystal growth from aqueous solution. J. L. Torgesen, A. T. Horton, and C. P. Saylor. (See above abstract.)

An automatic multichannel correlator. R. F. Brown, Jr. (See above abstract.)

Elastic constant—porosity relations for polycrystalline thoria. S. Spinner, F. P. Knudsen, and L. Stone. (See above abstract.)

An oxygen partial pressure warning instrument. L. Greenspan.

New fast-opening, large-aperture shutter for high-speed photography. E. C. Cassidy and D. H. Tsai. (See above abstract.)

Equations for the radiofrequency magnetic permeameter. C. A. Hoer and A. L. Rasmussen.

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WWV reception in the arctic during ionospheric disturbances. G. E. Hill and J. R. Herman.

Height-gain for VLF radio waves. J. R. Wait and K. P. Spies.

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