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Evaluation of the four elastic constants of some cubic crystals

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1. Introduction

The mathematical theory of elasticity in its generally accepted form derives from a memoir by A L Cauchy presented to the Academy of Sciences at Paris in 1822. The analytical specification of the strains and stresses in elastic solids adopted in that theory expresses the strains in terms of the differential displacements of neighbouring points in the solid and the stresses in terms of the tractive forces on infinitesimal areas in the same location. The theory, however, does not make use of these representations with complete generality, but following Cauchy, adopts them in modified forms on the basis of arguments put forward by him and considered as authoritative ever since. But when one examines those arguments critically, they are found to be indefensible. This is particularly clear in regard to the representation of strains. In the most general case, we have nine components of strain, but Cauchy reduced their number to six by eliminating movements which he identified with rigid body rotations. Actually, however, the components thus eliminated are not rigid body rotations, but differential rotations which are of the same nature as those appearing in the deformation of solids by torsion or flexure and hence, their elimination is not justified. Then again, Cauchy's reduction in the number of the stress components from nine to six is based on the idea that the angular momenta of the tractions taken about each of the co-ordinate axes and summed up should cancel out. But since the stresses are assumed to be in the nature of tractive forces and defined in terms of their magnitudes over infinitesimal areas, they have to be considered as acting on volume elements which are small enough to be regarded as particles and hence no consideration of angular momenta is called for. The reduction in number of the components of stress from nine to six has therefore no justification. Indeed, when once it is admitted that we have to retain all the nine components of strain, a similar step in regard to the components of stress follows inevitably.

In a recent paper (Raman and Viswanathan, 1955) the consequences of adopting the representations of stress and strain in elastic solids in their most general form have been discussed in detail. It has been shown in that paper that Cauchy's assumptions result in restricting the cases which fall within its scope to homogeneous strains properly-so-called. The more general case of heterogeneous strains, including especially all cases of wave-propagation and static deformations in the nature of torsion and flexure, lie outside its scope. Nevertheless, the mathematical theory of elasticity has actually been applied to these cases and formulae have been obtained and the constants appearing in them have been evaluated experimentally. For example, the results of experimental studies with cubic crystals have been expressed in terms of three constants usually designated as C_{11}, C_{12} and C_{44} respectively. On the other hand, the more general theory shows that four constants designated as d_{11}, d_{12}, d_{44} and d_{45} are needed for the classes O*h* and T*d* of the cubic system. Hence, by an examination of the experimental data for those cubic crystals of the O*h* and T*d* classes which have been investigated with adequate precision by different methods, it should be possible to decide whether those data are expressible in terms of three constants only, or whether four constants are actually needed. It is the object of the present paper to present the results of such an examination.

2. Some general remarks

The determination of elastic constants of crystals can be made independently by static and dynamic methods. In the former case we naturally deal with the elastic constants under isothermal conditions and in the latter case under adiabatic conditions. The dynamic methods depend upon the determination of velocity of propagation of high-frequency waves of different types in the solid. Many of the recent determinations of the elastic constants of crystals have been made by these methods and it would seem that a high degree of precision has been attained in the resulting data. We shall accordingly make use of them in the evaluation of the elastic constants of the respective materials.

The classical expression for the velocity of propagation in a cubic crystal in the older theory is given by equations of the type

$$\rho v^2 A^x = A^x\{C_{11}l^2 + C_{44}(m^2+n^2)\} + (C_{12}+C_{44})(A^y lm + A^z ln)$$

while in the corrected theory it is given by equations of the type

$$\rho v^2 A^x = A^x\{d_{11}l^2 + d_{44}(m^2+n^2)\} + (d_{12}+d_{45})(A^y lm + A^z ln).$$

Thus in reducing the experimental data we make the following identifications:

$$d_{11} = C_{11}; \quad d_{44} = C_{44} \quad \text{and} \quad (d_{12}+d_{45}) = (C_{12}+C_{44}).$$

It will be seen at once that if $d_{44} = d_{45}$, then the two theories lead to identical results.

Whereas in the older theory, if the wave-velocities had been measured for a sufficient number of directions the data resulting would suffice to determine the constants C_{11}, C_{12} and C_{44}, in the present theory it only enables us to evaluate the three quantities d_{11}, d_{44} and $(d_{12}+d_{45})$. Thus, at least one additional determination is needed by static methods yielding values for a different linear combination of the four constants. The most appropriate determination appears to be the bulk modulus the expression for which under the older theory is $(C_{11}+2C_{12})/3$, whereas in the new theory it is $(d_{11}+2d_{12})/3$. While determinations of the bulk modulus are not easy, there is reason to believe that a degree of precision adequate for our present purpose has been reached in the measurements made and reported from Bridgman's laboratory at Harvard. It is obvious that to utilize these data in conjunction with the determinations by the dynamic methods, it is necessary to assume that we are dealing in both cases with the same material and under the same physical conditions. Such an assumption would appear *prima facie* justifiable in the cases considered in the present paper, viz., crystallised solids of very simple chemical composition. The correctness of the assumption is reinforced by an intercomparison of the elastic constants determined by dynamic methods and reported by different authors from different laboratories. In general, these values do not differ more than can reasonably be ascribed to inevitable uncertainties in the experimental determinations.

Some further remarks are also necessary in this connection. Since the experimental values for the compressibility refer to isothermal conditions it is necessary to correct them to obtain its value under adiabatic conditions in order that a comparison might be possible with the adiabatic constants determined by dynamic methods. This correction is effected making use of the well known formula

$$\chi_{\mathrm{iso}} - \chi_{\mathrm{adia}} = \frac{9\alpha^2 T}{\rho C_p}$$

where χ represents the compressibility, α the coefficient of linear expansion of the substance, T the absolute temperature, ρ the specific gravity of the solid and C_p the specific heat of the solid in ergs per gram. The numerical values of the constants used in the calculation of this correction term have been taken from the *Landolt–Bornstein Tables* and the *International Critical Tables.*

The compressibility determinations made in Bridgman's laboratory usually extended upto very high pressures. We naturally make use of the compressibility value for zero pressures computed by the investigators themselves from the experimental data. The values reported by Bridgman and Slater prior to 1946 are subject to correction by a constant term $-0{\cdot}033 \times 10^{-7}\,kg^{-1}\,\mathrm{cm}^2$ in the light of Bridgman's latest determination of the linear compressibility of iron. Since the compressibility as well as the other elastic constants are functions of temperature, it is necessary that the comparison should be made for their values at the same temperature, either as reported by the authors themselves or as reduced to the same temperature from a knowledge of the variation of the elastic constants with temperature.

In selecting the substances the data for which are discussed in the present paper, the choice has naturally fallen on those substances which have been frequently the subject of experimental study. It so happens that these substances also fall into well-defined groups being very similar in chemical composition and their crystal structure, e.g., NaCl, KCl, KBr, NaBr, LiF, MgO and AgCl, all of which have the rock-salt structure; diamond, silicon, germanium, zinc blende and fluorspar all of which again have closely similar structures and finally the metallic elements aluminium, copper, nickel and silver which have the face-centred cubic structure. In tabulating our final results we have arranged the substances in the order stated, in order to facilitate intercomposition of their elastic behaviour.

3. Crystals with the rock-salt structure

(*a*) *Rock-salt*—The elastic constants of NaCl were determined by Voigt first in 1888 by the methods of torsion and flexure. Bridgman has also in 1929 determined the constants by the same methods. With the development of techniques based on ultrasonic wave-propagation, several determinations have been made recently by numerous investigators namely, Bergmann, Rose, Durand, Hunter and Siegel, Huntington, Galt, Lazarus and Bhagavantam. The values reported by these investigators and the methods used by them are given in table 1.

The values for C_{12} reported by the investigators who have used the static methods are distinctly higher than the values for the same constant obtained using dynamic methods, and this difference appears to be larger than can be reasonably ascribed to experimental errors. On the other hand, the values for C_{11} and C_{44} do not exhibit such a difference. The close agreement between the results

Table 1

Author	Method	C_{11}	C_{12}	C_{44}
Voigt	Static	4·77	1·32	1·29
Bridgman	”	4·94	1·37	1·28
Bergmann	Diffraction patterns	4·77	1·25	1·21
Rose (270° K)	Composite oscillator	5·06	1·30	1·278
Durand (300° K)	”	4·96	1·31	1·268
Hunter and Siegel	”	4·86	1·194	1·281
Huntington (25° C)	Pulse	4·85	1·23	1·265
Galt (298° K)	”	4·87	1·24	1·260
Lazarus (298° K)	”	4·911	1·225	1·284
Bhagavantam (R.T.)	Ultrasonic	4·97	1·27	1·27

reported by the three investigators who have used the pulse technique indicate that this method yields precise results. Hence, the mean of the values reported by these three workers have been adopted here as the best values.

The isothermal compressibility had been determined by static methods by a series of investigators, viz., Rontgen and Schneider, Madelung and Fuchs, Richards and Jones, Adams, Williamson and Johnston, Slater and Bridgman. Table 2 shows the values reported by the various authors. Of these, the most accurate are evidently those reported by Slater and Bridgman, and they have accordingly been adopted as correct. The values reported by Madelung and Fuchs refer to the pressure range 50–200 kg/cm², those of Richards and Jones to the range 100–510 kg/cm². The values of Slater and Bridgman quoted are for zero pressure always.

Table 2

Author	Temp.	χ in $10^{-7}\,kg^{-1}\,cm^2$
Rontgen and Schneider	R.T.	50
Madelung and Fuchs	0° C	40·5
Richards and Jones	20° C	44·0
Adams, Williamson and Johnston	R.T.	40·4
Slater	30° C	41·8
Bridgman	30° C	41·82
	75° C	43·44

These values are however subject to correction by a constant term $-0{\cdot}033 \times 10^{-7}\,kg^{-1}\,cm^2$ in the light of Bridgman's latest determination of the linear compressibility of iron. After making this correction and using the known value of g at Harvard, the isothermal compressibility of rock-salt comes out as $42{\cdot}62 \times 10^{-13}\,cm^2/dyne$ at 30° C. The value of the compressibility at 25° C is found by linear interpolation from the values reported by him at 30° C and 75° C. This correction when effected leads to a value of χ (isothermal) $= 42{\cdot}44$. The difference between the isothermal and adiabatic compressibilities can be calculated from the formula given earlier. For rock-salt, the numerical values used in the formula are: $\alpha = 44 \times 10^{-6}$; $\rho \doteq 2{\cdot}168$; $C_p = 0{\cdot}2078$ cal/gm. The value of the adiabatic compressibility at 25° C is found to be $39{\cdot}68 \times 10^{-13}\,cm^2/dyne$. Hence the bulk modulus comes out as $2{\cdot}52 \times 10^{11}$ dynes/cm². On the other hand, the value for the bulk modulus calculated from the formula $(C_{11} + 2C_{12})/3$ comes out at $2{\cdot}45 \times 10^{11}$ dynes/cm² the difference clearly being greater than can be explained in terms of experimental errors. The average values of the dynamically determined constants used in the calculation are: $C_{11} = 4{\cdot}877$; $C_{12} = 1{\cdot}232$; $C_{44} = 1{\cdot}269 \times 10^{11}$ dynes/cm², while the four constants evaluated in the manner already explained come out as $d_{11} = 4{\cdot}88$; $d_{12} = 1{\cdot}34$; $d_{44} = 1{\cdot}27$; and $d_{45} = 1{\cdot}16 \times 10^{11}$ dynes/cm².

(*b*) *Potassium chloride*—The elastic constants of KCl have been determined by static methods by Voigt, Forsterling and Bridgman. The later workers who have determined the elastic constants by the dynamic methods of ultrasonics are Durand, Galt and recently Lazarus. Their values appear in table 3.

It will be noticed from table 3 that the values reported by the different authors are in much less satisfactory agreement amongst themselves than in the case of rock-salt. The values for C_{12} in particular appear rather erratic and this is probably due to the fact that measurements usually involve the determination of linear combinations of C_{11} and C_{12} and since C_{12} is much smaller of the two, errors of measurement would influence its determined value very noticeably. Voigt gives C_{12} to three significant figures but his value is undoubtably an error. As in the case of rock-salt we shall assume as a definitive value the mean of the measurements by the pulse method at 25° C.

Table 3

Author		Method	C_{11}	C_{12}	C_{44}
Voigt	R.T.	Static	3·75	0·198	0·655
Forsterling	R.T.	"	3.88	0·640	0·65
Bridgman	30° C	"	3·70	0·81	0·79
Durand	R.T.	Composite oscillator	4·00	0·6	0·625
Galt	25° C	Pulse	3·98	0·625	0·62
Lazarus	25° C	"	4·095	0·705	0·630

The static measurements of compressibilities by different authors shown in table 4 agree remarkably well amongst themselves. We shall here accept the measurement by Slater as corrected by Bridgman to be the most reliable. This comes out as $56{\cdot}27 \times 10^{-13}$ dynes^{-1} cm^2 at 30° C and after correction using the temperature coefficient given by Slater, the value at 25° C is found as $56{\cdot}14 \times 10^{-13}$ cm^2/dyne. From this the adiabatic compressibility at 25° C is calculated using the following values for KCl in the correction formula.

Table 4

Author	Temp.	χ in 10^{-7} kg^{-1} cm^2
Röntgen and Schneider	—	56
Madelung and Fuchs	0° C	55·1
Richards and Jones	20° C	53·0
Slater	30° C	55·2

$\alpha = 36 \times 10^{-6}$; $\rho = 1{\cdot}992$; and $C_p = 0{\cdot}1661$ cal/gm. The adiabatic compressibility is found to have a value $53{\cdot}62 \times 10^{-13}$. Hence the bulk modulus at 25° C comes out as $1{\cdot}865 \times 10^{11}$ dynes/cm^2.

The mean values for C_{11}, C_{12} and C_{44} adopted are 4·038, 0·663 and 0·628 $\times 10^{11}$ respectively. The bulk-modulus calculated using the classical expression $(C_{11} + 2C_{12})/3$ comes out as $1{\cdot}788 \times 10^{11}$ dynes/cm^2, which is definitely smaller than the experimentally determined value. The values found for the four elastic constants of the new theory are respectively: $d_{11} = 4{\cdot}038$; $d_{12} = 0{\cdot}799$; $d_{44} = 0{\cdot}628$; $d_{45} = 0{\cdot}512 \times 10^{11}$ dynes/cm^2.

(*c*) *Potassium bromide*—Static measurements of the elastic constants have been reported by Bridgman. Using the pulse technique Huntington and Galt have independently determined the constants at room temperature. The values are given in table 5.

Table 5

Author		Method	C_{11}	C_{12} $\times 10^{11}$ dynes/cm^2	C_{44}
Bridgman	30° C	Static	3·33	0·58	0·62
Huntington	25° C	Pulse	3·45	0·54	0·508
Galt	25° C	”	3·46	0·58	0·505

The compressibility measurements have been made by Richards and Jones, and Slater independently and the values reported are $6{\cdot}5 \times 10^{-6}$ kg^{-1} cm^2 at 20° C and $6{\cdot}57 \times 10^{-6}$ kg^{-1} cm^2 at 30° C respectively, being in good agreement with each other. Using the temperature coefficient given by Slater, the isothermal compressibility at 25° C on calculation is found to be $66{\cdot}78 \times 10^{-13}$ cm^2 dyne^{-1}. The adiabatic compressibility is found using the correction formula given earlier. The values adopted for KBr are: $\alpha = 41 \times 10^{-6}$; $\rho = 2{\cdot}756$; $C_p = 0{\cdot}1033$ cal./gm. $\chi_{(\mathrm{adiabatic})}$ comes out as $62{\cdot}99 \times 10^{-13}$ cm^2/dyne and hence the bulk modulus is $1{\cdot}588 \times 10^{11}$ dynes/cm^2 at 25° C.

Adopting the mean of the values given by Galt and Huntington the bulk modulus in terms of the classical formula $(C_{11} + 2C_{12})/3$ is found to be 1·525 $\times 10^{11}$ dynes/cm^2, thus differing from the actually observed value corrected for the adiabatic nature of deformation.

The values adopted for the elastic constants are $C_{11} = 3{\cdot}455$, $C_{12} = 0{\cdot}56$, $C_{44} = 0{\cdot}507$, while the four constants evaluated in the manner explained are $d_{11} = 3{\cdot}455$; $d_{12} = 0{\cdot}655$; $d_{44} = 0{\cdot}507$; $d_{45} = 0{\cdot}412 \times 10^{11}$ dynes/cm^2.

(*d*) *Sodium bromide*—The static measurements of the elastic constants are due to Bridgman, while they have been determined by Bhagavantam using ultrasonic methods.

Table 6

Author	Temp.	C_{11}	C_{12}	C_{44}
Bridgman	30° C	3·30	1·31	1·33
Bhagavantam	R.T.	3·87	0·97	0·97

The values reported by Bhagavantam differ appreciably from those of Bridgman. However, we shall take for our calculations the values determined by dynamic methods as usual, since the identification of the constants of the new theory with that of the older theory is by identifying the two wave-equations.

The compressibility determinations in the case of NaBr have been made by Richards and Saerens at 20° C, the value being $5{\cdot}4 \times 10^{-6}\,\mathrm{kg}^{-1}\,\mathrm{cm}^2$ in the pressure range 100–510 kg/cm^2, and by Slater at 30° C who reports a zero pressure value of $4{\cdot}98 \times 10^{-6}\,\mathrm{kg}^{-1}\,\mathrm{cm}^2$. The isothermal compressibility at 30° C is found to be $50{\cdot}762 \times 10^{-13}$ cm^2/dyne. Correcting this to the adiabatic value we get $\chi_{(\mathrm{adiabatic})}$ as 47·576. The values used in the calculation of the correction term are: $\alpha = 43 \times 10^{-6}$; $\rho = 3{\cdot}213$; $C_p = 0{\cdot}1178$ cal/gm. The bulk modulus value hence comes out as $2{\cdot}102 \times 10^{11}$ dynes/cm^2 whereas according to the classical theory this value should be $1{\cdot}936 \times 10^{11}$ dynes/cm^2.

The values of the elastic constants according to the new theory are: $d_{11} = 3{\cdot}87$; $d_{12} = 1{\cdot}22$; $d_{44} = 0{\cdot}97$; $d_{45} = 0{\cdot}72 \times 10^{11}$ dynes/cm^2.

(*e*) *Lithium fluoride*—The elastic constants of LiF have been determined by dynamic methods by Bergmann, Huntington, Sundara Rao and Seshagiri Rao and their values are shown in table 7.

Table 7

Author		Method	C_{11}	C_{12}	C_{44}
Bergman	R.T.	Diffraction patterns	12·0	4·41	6·4
Huntington	25° C	Pulse	9·74	4·04	5·54
Sundara Rao	R.T.	Ultrasonic	11·9	4·58	5·42
Seshagiri Rao	R.T.	"	11·9	5·38	5·34

It will be noticed that there are notable divergences between the values reported by different investigators though they all use ultrasonic methods. A clue to the origin of these differences is to be found in the differences in density reported by the different investigators in their respective papers. The density of

LiF calculated from the lattice spacing and known atomic weights is 2·627, while Huntington, Seshagiri Rao and Sundara Rao give the density as 2·295, 2·635 and 2·601 respectively. The value found in Landolt Bornstein Table is 2·640. As the value reported by Seshagiri Rao corresponds to this, we use his data in our calculations.

The compressibility of LiF has been determined by Slater as 15·3 × 10^{-7} kg^{-1} cm^2 at 30° C and in a redetermination Bridgman has corrected this value and gives it as 14·95 × 10^{-7} kg^{-1} cm^2. The isothermal compressibility at 30° C is accordingly 15·215 × 10^{-13} cm^2 $dyne^{-1}$. The following values are used in the correction term for adiabatic compressibility; $\alpha = 36 \times 10^{-6}$; $\rho = 2{\cdot}64$; and $C_p = 0{\cdot}373$ cal/gm. The adiabatic compressibility comes out as 14·357 × 10^{-13} and hence the bulk modulus as 6·965 × 10^{11} dynes/cm^2, while the bulk modulus using the data of Seshagiri Rao and the classical formula $(C_{11} + 2C_{12})/3$ is found to be having a different value of 7·55 × 10^{11} dynes/cm^2. Using the values of Seshagiri Rao in our calculation we find the following values for the four elastic constants. $d_{11} = 11{\cdot}9$; $d_{12} = 4{\cdot}5$; $d_{44} = 5{\cdot}34$; and $d_{45} = 6{\cdot}22 \times 10^{11}$ dynes/cm^2.

(*f*) *Magnesium oxide*—The elastic constants of MgO have been determined dynamically by Durand and by Bhagavantam and their values are shown below.

Table 8

Author		C_{11}	C_{12}	C_{44}
Durand	30°C	28·92	8·77	14·47
Bhagavantam	R.T.	28·6	8·7	14·8

Their values agree fairly well and the slight difference in the value of C_{44} might be due to experimental errors. No static determinations of the elastic constants appear to have been made.

The compressibility of MgO has been determined by Madelung and Fuchs and by Bridgman. The former investigators report varying values with the different specimens they used, while Bridgman using a clear single crystal has reported the value of 5·904 × 10^{-7} kg^{-1} cm^2 at 30° C. The isothermal compressibility at 30° C is hence 5·988 × 10^{-13} cm^2/dyne. The values of the constants appearing in the correction term are: $\alpha = 13{\cdot}3 \times 10^{-6}$; $\rho = 3{\cdot}576$; $C_p = 0{\cdot}2297$ cal/gm. The adiabatic compressibility comes out as 5·847 × 10^{-13} and hence the bulk modulus as 17·10 × 10^{11} dynes/cm^2.

We shall make use of the mean of the two dynamic determinations for the purposes of our calculation, i.e., $C_{11} = 28{\cdot}76$; $C_{12} = 8{\cdot}74$ and $C_{44} = 15{\cdot}14$. The compressibility calculated using the formula $(C_{11} + 2C_{12})/3$ is found to be equal to 15·41 × 10^{11} dynes/cm^2, being distinctly different from the observed and corrected value of 17·10 × 10^{11}. The elastic constants according to the new theory are as follows: $d_{11} = 28{\cdot}76$; $d_{12} = 11{\cdot}27$; $d_{44} = 15{\cdot}14$; $d_{45} = 12{\cdot}61 \times 10^{11}$ dynes/cm^2.

(*g*) *Silver chloride*—The elastic constants of AgCl have been recently determined using the pulse method by Arenberg (1950). The values have been reported for two different specimens and show good agreement between themselves. However, it is stated by him that the values from one of the specimens are to be preferred and they are given as $C_{11} = 6{\cdot}05$; $C_{12} = 3{\cdot}64$. $C_{44} = 0{\cdot}624 \times 10^{11}$ dynes/cm^2. The compressibility of fused and solidified AgCl has been determined by Richards and Jones, while Bridgman has studied the case of AgCl with compressed powder. The isothermal bulk-modulus value of $4{\cdot}12 \times 10^{11}$ obtained by extrapolating Bridgman's data to zero pressure agrees well with the value of $4{\cdot}17 \times 10^{11}$ dynes/cm^2 reported by Richards and Jones. Adopting the value due to Bridgman and using the values $\alpha = 30 \times 10^{-6}$; $\rho = 5{\cdot}5$; and $C_p = 0{\cdot}0875$ cal/gm. for AgCl, the adiabatic bulk modulus is found to be $4{\cdot}338 \times 10^{11}$ dynes/cm^2. According to the classical formula $(C_{11} + 2C_{12})/3$ this value comes out as $4{\cdot}444 \times 10^{11}$ dynes/cm^2, being different from the value given above. The four elastic constants according to the new theory are: $d_{11} = 6{\cdot}05$; $d_{12} = 3{\cdot}482$; $d_{44} = 0{\cdot}624$; $d_{45} = 0{\cdot}782 \times 10^{11}$ dynes/cm^2.

4. Crystals with the diamond-like structure

(*a*) *Diamond*—The elastic constants of diamond have been determined by the ultrasonic wedge method by Bhagavantam and Bhimasenachar (1946). The following are the values reported by them. $C_{11} = 9{\cdot}5 \times 10^{12}$; $C_{12} = 3{\cdot}9 \times 10^{12}$ and $C_{44} = 4{\cdot}3 \times 10^{12}$ dynes/cm^2. The compressibility has been determined first by Adams and again by Williamson in the same laboratory, the values being $0{\cdot}16 \times 10^{-12}$ and $0{\cdot}18 \times 10^{-12}$ cm^2/dyne respectively. The latter value is reported to be preferred since better material was used in the determination by Williamson. This gives a value of $5{\cdot}56 \times 10^{12}$ dynes/cm^2 for the isothermal bulk modulus. The correction for the adiabatic bulk modulus is negligible. Using this value of $5{\cdot}56 \times 10^{12}$ and the reported values for the elastic constants the values of the four elastic constants are calculated. They are: $d_{11} = 9{\cdot}5$; $d_{12} = 3{\cdot}59$; $d_{44} = 4{\cdot}30$; and $d_{45} = 4{\cdot}61 \times 10^{12}$ dynes/cm^2.

(*b*) *Germanium*—The elastic constants of Ge have been determined by ultrasonic methods by Bond and others, Fine and McSkimin and their values are shown in table 9.

All the determinations have been made in the Bell Telephone Laboratories and McSkimin and Fine have studied the variations of the constants with temperature. The values show good agreement between themselves. The values due to

Table 9

Author		Method	C_{11}	C_{12}	C_{44}
Bond and others	25°C	Pulse	12·90	4·84	6·69
Fine	25°C	Composite oscillator	13·16	5·09	6·69
McSkimin	30°C	Pulse	12·88	4·825	6·705

McSkimin are taken from the graphs given by him exhibiting the variation of the elastic constants with temperature.

The compressibility of *polycrystalline* germanium has been determined by Bridgman at 30° C on two occasions with different specimens and the values are $13{\cdot}78 \times 10^{-7}\,\mathrm{kg}^{-1}\,\mathrm{cm}^2$ and $14{\cdot}11 \times 10^{-7}\,\mathrm{kg}^{-1}\,\mathrm{cm}^2$ and the latter value is said to be more reliable. The isothermal compressibility at 30° C is hence $14{\cdot}358 \times 10^{-13}\,\mathrm{cm}^2/\mathrm{dyne}$. The constants used in the correction term to find the adiabatic compressibility are: $\alpha = 5{\cdot}5 \times 10^{-6}$; $\rho = 5{\cdot}323$; $C_p \doteq 22{\cdot}3$ Joules/gm atom. The corrected value of the adiabatic compressibility is $14{\cdot}308 \times 10^{-13}\,\mathrm{cm}^2/\mathrm{dyne}$ and hence the bulk modulus value is $6{\cdot}989 \times 10^{11}$ dynes/cm^2.

The elastic constants for 30° C could be more accurately and directly obtained from McSkimin's detailed data. Using his values we find that the bulk modulus value according to the classical formula should be $7{\cdot}51 \times 10^{11}$ dynes/cm^2. The four elastic constants are found to be $d_{11} = 12{\cdot}88$; $d_{12} = 4{\cdot}04$; $d_{44} = 6{\cdot}705$; and $d_{45} = 7{\cdot}49 \times 10^{11}$ dynes/cm^2.

(*c*) *Silicon*—The elastic constants of crystalline silicon have been determined by McSkimin and others and subsequently in detail by McSkimin over a wide range of temperatures. The following values for the constants at 30° C are found from the graphs given by him. $C_{11} = 16{\cdot}56$; $C_{12} = 6{\cdot}386$; $C_{44} = 7{\cdot}953 \times 10^{11}$ dynes/cm^2. The compressibility of *polycrystalline* silicon has been determined over a wide range of pressures by Bridgman at 30°C and on extrapolating his values to zero pressure, the isothermal compressibility is found to be $9{\cdot}92 \times 10^{-7}\,\mathrm{kg}^{-1}\,\mathrm{cm}^2$, i.e., $10{\cdot}118 \times 10^{-13}\,\mathrm{dynes}^{-1}\,\mathrm{cm}^2$. The following values are used in the correction term for adiabatic compressibility. $\alpha = 2{\cdot}25 \times 10^{-6}$; $\rho = 2{\cdot}331$; $C_p = 0{\cdot}1712$ cal/gm. On correction the adiabatic compressibility is found to be $10{\cdot}11 \times 10^{-13}\,\mathrm{dynes}^{-1}\,\mathrm{cm}^2$ and hence the bulk modulus as $9{\cdot}89 \times 10^{11}$ dynes/cm^2. The value calculated using the formula $(C_{11} + 2C_{12})/3$ is found to be $9{\cdot}78 \times 10^{11}$ dynes/cm^2. The four elastic constants calculated are: $d_{11} = 16{\cdot}56$; $d_{12} = 6{\cdot}56$; $d_{44} = 7{\cdot}953$; and $d_{45} = 7{\cdot}78 \times 10^{11}$ dynes/cm^2.

(*d*) *Zinc blende*—The elastic constants of zinc blende have been reported by Bhagavantam and Suryanarayana using ultrasonic methods. The constant C_{44} has however been obtained by them from static torsion experiments. The crystalline material used by them contained only 94% of zinc sulphide. The following values are reported by them. $C_{11} = 10{\cdot}79 \times 10^{11}$; $C_{12} = 7{\cdot}22 \times 10^{11}$; $C_{44} = 4{\cdot}12 \times 10^{11}$. These values are in disagreement with the values reported by Voigt from static methods, which are: $C_{11} = 9{\cdot}43 \times 10^{11}$; $C_{12} = 5{\cdot}68 \times 10^{11}$; $C_{44} = 4{\cdot}37 \times 10^{11}$.

The compressibility of a single crystal of zinc blende has been determined by Bridgman as $12{\cdot}81 \times 10^{-7}\,\mathrm{kg}^{-1}\,\mathrm{cm}^2$ at 30° C. This gives a value of $13{\cdot}032 \times 10^{-13}\,\mathrm{dynes}^{-1}\,\mathrm{cm}^2$ at 30° C for the isothermal compressibility. The constants used in the correction term for adiabatic compressibility are: $\alpha = 6{\cdot}7 \times 10^{-6}$; $\rho = 4{\cdot}102$; and $C_p = 0{\cdot}1146$ cal/gm. The corrected value of the adiabatic compressibility is found to be $12{\cdot}97 \times 10^{-13}\,\mathrm{dynes}^{-1}\,\mathrm{cm}^2$, and hence the bulk modulus is $7{\cdot}71 \times 10^{11}$ dynes/cm². The bulk-modulus calculated from the formula $(C_{11} + 2C_{12})/3$ using Bhagavantam and Suryanarayana's values is $8{\cdot}41 \times 10^{11}$ whereas Voigt's values give $6{\cdot}93 \times 10^{11}$ dynes/cm².

In the calculation of the four elastic constants, we make use of Bhagavantam and Suryanarayana's values since they are for the major part obtained from dynamic methods. We obtain the following values for the constants. $d_{11} = 10{\cdot}79$; $d_{12} = 6{\cdot}17$; $d_{44} = 4{\cdot}12$; and $d_{45} = 5{\cdot}17 \times 10^{11}$ dynes/cm².

(*e*) *Fluorspar*—The elastic constants of fluorspar have been determined using static methods by Voigt, and by Bergmann and Bhagavantam using dynamic methods. Their values are shown in table 10.

Table 10

Author	Method	C_{11}	C_{12}	C_{44}
Voigt	Static	16·4	4·47	3·38
Bergmann	Diffraction patterns	16·76	4·72	3·69
Bhagavantam	Ultrasonic	16·44	5·02	3·47

For our calculations we take here the mean of the values of Bergmann and Bhagavantam, i.e., $C_{11} = 16{\cdot}6$; $C_{12} = 4{\cdot}87$; and $C_{44} = 3{\cdot}58 \times 10^{11}$ dynes/cm².

The compressibility of CaF_2 has been determined by Madelung and Fuchs at 0° C and in the pressure range 50–200 kg/cm² and the value reported by them is $12{\cdot}2 \times 10^{-7}\,\mathrm{kg}^{-1}\,\mathrm{cm}^2$. Bridgman has also determined the compressibility at 30° C and reports a zero pressure value of $12{\cdot}06 \times 10^{-7}\,\mathrm{kg}^{-1}\,\mathrm{cm}^2$, i.e., $12{\cdot}267 \times 10^{-13}$ cm²/dyne. The values used in the correction term are: $\alpha = 19{\cdot}11 \times 10^{-6}$; $\rho = 3{\cdot}18$; $C_p = 0{\cdot}887$ Joules/gm. The adiabatic compressibility value is found to be $11{\cdot}914 \times 10^{-13}$ cm²/dyne and hence the bulk modulus is $8{\cdot}39 \times 10^{11}$ dynes/cm². The bulk modulus value using the formula $(C_{11} + 2C_{12})/3$ is found to be $8{\cdot}78 \times 10^{11}$ dynes/cm².

The four elastic constants calculated are: $d_{11} = 16{\cdot}6$; $d_{12} = 4{\cdot}29$; $d_{44} = 3{\cdot}58$; and $d_{45} = 4{\cdot}16 \times 10^{11}$ dynes/cm².

5. Metals crystallizing in the cubic system

(*a*) *Aluminium*—The elastic constants of single crystals of aluminium have been determined using static methods of Goens. Recently Lazarus and Sutton have independently measured the elastic constants by ultrasonic methods. The values reported by all these investigators are shown in table 11.

The accuracy in the measurements of Lazarus is greater than that of Sutton as is evidenced by the comments made by them in their respective papers. Moreover the purity of the specimens used by Lazarus and Sutton is given as 99·99% and 99·93% respectively. In view of these facts we take Lazarus's values for the purposes of our calculation.

Table 11

Author		Method	C_{11}	C_{12}	C_{44}
Goens	R.T.	Static	10·82	6·22	2·84
Lazarus	25° C	Pulse	10·56	6·39	2·853
Sutton	20° C	Composite oscillator	11·29	6·65	2·783

The isothermal compressibility of aluminium single crystals has been determined by Bridgman as $13{\cdot}38 \times 10^{-7}\,\mathrm{kg}^{-1}\,\mathrm{cm}^2$ at 30° C and as $13{\cdot}76 \times 10^{-7}\,\mathrm{kg}^{-1}\,\mathrm{cm}^2$ at 75° C. The value at 25° C on linear extrapolation comes out as $13{\cdot}338 \times 10^{-7}\,\mathrm{kg}^{-1}\,\mathrm{cm}^2$, i.e., $13{\cdot}57 \times 10^{-13}\,\mathrm{dynes}^{-1}\,\mathrm{cm}^2$. The following values for the constants are used in the correction term for adiabatic compressibility: $\alpha = 23{\cdot}06 \times 10^{-6}$; $\rho = 2{\cdot}702$; $C_p = 0{\cdot}2129$ cal/gm. The adiabatic compressibility is found to be $12{\cdot}97 \times 10^{-13}\,\mathrm{dynes}^{-1}\,\mathrm{cm}^2$ and hence the bulk modulus is $7{\cdot}71 \times 10^{11}$ dynes/cm². The bulk modulus obtained from the values of Lazarus is $7{\cdot}78 \times 10^{11}$. The values of the four elastic constants calculated are: $d_{11} = 10{\cdot}56$; $d_{12} = 6{\cdot}29$; $d_{44} = 2{\cdot}853$; $d_{45} = 2{\cdot}953 \times 10^{11}$ dynes/cm².

(*b*) *Copper*—The elastic constants of copper single crystals have been determined using the composite oscillator method by Goens and Weerts. Recently Lazarus, Long, and Overton and Gaffney have determined the constants using pulse methods. The values are shown in table 12.

Table 12

Author		Method	C_{11}	C_{12}	C_{44}
Goens and Weerts	R.T.	Composite oscillator	16·98	12·26	7·53
Lazarus	25° C	Pulse	17·1	12·39	7·56
Long	300° K	"	16·83	12·21	7·54
Overton and Gaffney	300° K	"	16·84	12·14	7·54

There is very good agreement between the three sets of values determined by the pulse method and hence for the purposes of our calculation we shall make use of the mean of these values.

The compressibility of polycrystalline copper of high purity has been determined by Bridgman as $7{\cdot}19 \times 10^{-7}$ kg^{-1} cm^2 at 30° C and $7{\cdot}34 \times 10^{-7}$ at 75° C. Hence the value at 300° K is found to be $7{\cdot}173 \times 10^{-7}$ kg^{-1} cm^2, i.e., $7{\cdot}283 \times 10^{-13}$ dynes^{-1} cm^2. The following values are used in the correction term for the adiabatic compressibility: $\alpha = 17{\cdot}09 \times 10^{-6}$; $\rho = 8{\cdot}92$; $C_p = 0{\cdot}0919$ cal/gm. The corrected value of adiabatic compressibility is $7{\cdot}05 \times 10^{-13}$ dynes^{-1} cm^2 and hence the bulk modulus is $14{\cdot}18 \times 10^{11}$ dynes/cm^2. The average values of the elastic constants from pulse method are: $C_{11} = 16{\cdot}92$; $C_{12} = 12{\cdot}25$ and $C_{44} = 7{\cdot}55 \times 10^{11}$ dynes/cm^2. The bulk modulus using the formula $(C_{11} + 2C_{12})/3$ is found to be $13{\cdot}81 \times 10^{11}$ dynes/cm^2. The four elastic constants calculated are: $d_{11} = 16{\cdot}92$; $d_{12} = 12{\cdot}81$; $d_{44} = 7{\cdot}55$; and $d_{45} = 6{\cdot}99 \times 10^{11}$ dynes/cm^2.

(*c*) *Nickel*—The elastic constants of single crystals of nickel have been determined recently using the ultrasonic pulse method by Bozorth and others and also by Neighbours and others. Their values are given in table 13.

Table 13

Author	C_{11}	C_{12} in 10^{12} dynes/cm^2	C_{44}
Bozorth and others	2·53	1·58	1·22
"	2·524	1·538	1·23
"	2·523	1·566	1·23
Neighbours and others	2·528	1·52	1·238

The average value of these at 25° C are: $C_{11} = 2{\cdot}526$; $C_{12} = 1{\cdot}551$; and $C_{44} = 1{\cdot}23 \times 10^{12}$ dynes/cm^2.

The compressibility of pure nickel has been determined by Bridgman at 30° C as $5{\cdot}29 \times 10^{-7}$ kg^{-1} cm^2 and at 75° C as $5{\cdot}35 \times 10^{-7}$. The value at 25° C is hence $5{\cdot}283 \times 10^{-7}$ kg^{-1} cm^2. The isothermal compressibility is hence $5{\cdot}355 \times 10^{-13}$ dynes^{-1} cm^2. The values used in the correction term for adiabatic compressibility are: $\alpha = 13{\cdot}15 \times 10^{-6}$; $\rho = 8{\cdot}9$; and $C_p = 0{\cdot}107$ cal/gm. The adiabatic compressibility is found to be $5{\cdot}239 \times 10^{-13}$ dynes^{-1} cm^2 and hence the bulk modulus is $19{\cdot}09 \times 10^{11}$ dynes/cm^2. The bulk modulus using the classical formula is found to be $18{\cdot}76 \times 10^{11}$ dynes/cm^2. The four elastic constants calculated are: $d_{11} = 25{\cdot}26$; $d_{12} = 16{\cdot}01$; $d_{44} = 12{\cdot}3$; and $d_{45} = 11{\cdot}8 \times 10^{11}$ dynes/cm^2.

(*d*) *Silver*—The elastic constants of single crystals of silver have been determined by Rohl using the classical static and dynamic methods. The constants have been recently determined by Bacon and Smith using the ultrasonic pulse method. The values are shown below.

Table 14

Author		Method	C_{11}	C_{12}	C_{44}
Rohl	R.T.	Static etc.	11·9	8·94	4·37
Bacon and Smith	R.T.	Pulse	12·4	9·34	4·61

The compressibility of pure silver has been determined by Bridgman at 30° C as $9{\cdot}87 \times 10^{-7}\,\mathrm{kg}^{-1}\,\mathrm{cm}^2$, i.e., $10{\cdot}034 \times 10^{-13}\,\mathrm{dynes}^{-1}\,\mathrm{cm}^2$. The constants used in the correction term are: $\alpha = 18{\cdot}9 \times 10^{-6}$; $\rho = 10{\cdot}5$; $C_p = 25{\cdot}2$ Joules/gm atom. The adiabatic compressibility is found to be $9{\cdot}939 \times 10^{-13}\,\mathrm{dynes}^{-1}\,\mathrm{cm}^2$ and hence the bulk modulus is $10{\cdot}06 \times 10^{11}$ dynes/cm^2. The value calculated using the formula $(C_{11} + 2C_{12})/3$ is found to be $10{\cdot}36 \times 10^{11}$ dynes/cm^2. The four constants calculated are: $d_{11} = 12{\cdot}4$; $d_{12} = 8{\cdot}89$; $d_{44} = 4{\cdot}61$; and $d_{45} = 5{\cdot}06 \times 10^{11}$ dynes/cm^2.

6. Some final remarks

In table 15 the results for the individual cases given in the foregoing pages have been collected together. The columns C_{11}, C_{12} and C_{44} show the results of the

Table 15. Elastic constants in 10^{11} dynes/cm^2

Substance	C_{11}	C_{12}	C_{44}	d_{11}	d_{12}	d_{44}	d_{45}
NaCl	4·877	1·232	1·269	4·877	1·34	1·269	1·16
KCl	4·038	0·663	0·628	4·038	0·779	0·628	0·512
KBr	3·455	0·56	0·507	3·455	0·655	0·507	0·412
NaBr	3·87	0·97	0·97	3·87	1·22	0·97	0·72
LiF	11·9	5·38	5·34	11·9	4·5	5·34	6·22
MgO	28·76	8·74	15·14	28·76	11·27	15·14	12·61
AgCl	6·05	3·64	0·624	6·05	3·482	0·624	0·782
Diamond	95	39	43	95	35·9	43·0	46·1
Ge	12·88	4·825	6·705	12·88	4·04	6·705	7·49
Si	16·56	6·386	7·953	16·56	6·56	7·953	7·78
ZnS	10·79	7·22	4·12	10·79	6·17	4·12	5·17
CaF_2	16·6	4·87	3·58	16·6	4·29	3·58	4·16
Al	10·56	6·39	2·853	10·56	6·29	2·853	2·953
Cu	16·92	12·25	7·55	16·92	12·81	7·55	6·99
Ni	25·26	15·51	12·3	25·26	16·01	12·3	11·8
Ag	12·4	9·34	4·61	12·4	8·89	4·61	5·06

ultrasonic measurements, while the columns d_{11}, d_{12}, d_{44} and d_{45} represents the constants as evaluated from the ultrasonic data in conjunction with the bulk modulus as determined by Bridgman and his collaborators after making *all* necessary corrections. The values of C_{11} and d_{11} are in each case identical; likewise those of C_{44} and d_{44}. But C_{12} and d_{12} are different and such difference is a measure of the failure of the three constant-theory to represent the actual elastic behaviour of the crystal. The difference between d_{44} and d_{45} also expresses the same situation in another way.

Certain general features emerge from the table. For all the four alkali halides which are soluble in water, C_{12} is less than d_{12} and likewise d_{45} is less than d_{44}. This regularity of behaviour taken in conjunction with the reliability of the data in these cases makes it clear that these differences are real and justify us in concluding that the elastic behaviour of cubic crystals cannot be expressed in terms of three constants, but needs four. Diamond, germanium, zinc blende and fluorspar also exhibit a parallel behaviour which is the reverse of that shown by the four water-soluble alkali halides. In their cases, C_{12} is decidedly greater than d_{12}, while *per contra* d_{44} is less than d_{45} and these differences are numerically more striking than in the case of the alkali halides. Magnesium oxide for which the data are reliable exhibits a noteworthy behaviour; the differences between C_{12} and d_{12} and likewise between d_{44} and d_{45} are in the same sense as in the alkali halides but proportionately much larger. Differences of the same order of magnitude but in the opposite sense are shown by lithium fluoride. In the case of the metals crystallising in the face-centred cubic system, we also find differences between C_{12} and d_{12} and between d_{44} and d_{45}, but they are not always in the same sense. This is a feature which need not surprise us in view of the very great differences exhibited by these metals in other respects.

7. Summary

The belief that the elastic behaviour of cubic crystals can be described in terms of three constants rests on theoretical considerations which are examined in the paper and shown to be indefensible. The correct theory demands four constants for cubic crystals belonging to the O_h and T_d classes. The experimental results for sixteen different crystals belonging to these classes for which the most precise data are available are critically examined and it is shown that the adiabatic bulk modulus as computed respectively from the observed velocities of ultrasonic wave propagation and from the static determinations of compressibility made at Harvard are in systematic disagreement. The data show very clearly that the elastic behaviour of these crystals cannot be expressed in terms of three constants, but needs four. The latter have been computed and tabulated.

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