Acta Cryst. (1953). **6**, 331

'Third-Order' Elastic Coefficients

By R. F. S. Hearmon

Physics Section, Forest Products Research Laboratory, Princes Risborough, Aylesbury, Bucks., England

(*Received* 14 *June* 1952 *and in revised form* 1 *October* 1952)

The definition of third-order elastic constants, and some of the properties of the associated tensors, are discussed. A direct enumeration of the third-order constants is made for all crystal classes, and for the isotropic system; estimates are given of the numerical values of certain combinations of third-order constants for five cubic materials.

1. Introduction

In the classical theory of elasticity, the strains are assumed to be infinitesimal, and the resulting strain energy function is a homogeneous quadratic function of the strains (Love, 1927). If the strains are not infinitesimal, then terms of the third and higher degree in the strains enter into the strain energy function (Kaplan, 1931). The energy of deformation of a body can then be written

$$\varphi = \varphi_0 + k_1 c_{ij}\eta_{ij} + k_2 c_{ijkl}\eta_{ij}\eta_{kl} + k_3 c_{ijklmn}\eta_{ij}\eta_{kl}\eta_{mn} + \ldots, \quad (1)$$

where η_{ij} are the Lagrangian strain components (Birch, 1947), and the c's are material constants. In order to conform with the usual definitions (Institute of Radio Engineers, 1949), k_2 must take the value $\frac{1}{2}$, and k_3 is here put equal to 1.

If the initial energy and the initial cubical dilatation of the body are zero, the first two terms in (1) are also zero (Murnaghan, 1951) and

$$\left.\begin{aligned}\varphi &= \tfrac{1}{2}c_{ijkl}\eta_{ij}\eta_{kl} + c_{ijklmn}\eta_{ij}\eta_{kl}\eta_{mn} + \ldots \\ &= \varphi_2 \qquad\qquad + \varphi_3 + \ldots\ .\end{aligned}\right\} \quad (2)$$

The c_{ijkl} are the elastic stiffnesses (I.R.E., 1949); they form a fourth-order tensor containing 81 components, of which 21 are independent for a triclinic material. As the symmetry of the material increases, the number of independent constants is reduced, until, for cubic and isotropic materials, the numbers are three and two respectively (Love, 1927).

The c_{ijklmn} are known as the 'third-order' elastic coefficients. They form a sixth-order tensor containing 729 components, of which 56 are independent for a triclinic material. Birch (1947) derived the schemes of independent coefficients for all classes of cubic crystals. He showed that some of these classes possess eight independent coefficients, and the remainder six. Later, Bhagavantam & Suryanarayana (1947, 1949) applied a group theoretical method to the determination of the numbers of independent third-order coefficients in each crystal class and corrected Birch's result for one of the cubic classes. Their predictions have been independently confirmed by Jahn (1949), who has also extended the calculations to include isotropic materials. The number of coefficients predicted by Jahn in this case is three, but Kaplan (1931) had previously investigated the form of the strain energy equation (2) for isotropic bodies, and had concluded that the number of independent third-order coefficients was two only. It may be noted here that the isotropic system actually contains two symmetry classes (Jahn, 1949), but that, from the point of view of elastic properties the two classes are indistinguishable.

While the present work was in progress, a number of workers have independently contributed towards the solution of the general problem of third-order elastic coefficients. Murnaghan (1951) has given the schemes of coefficients corresponding with simple two- and four-fold rotation axes, and has indicated in principle a method for dealing with three- and six-fold axes. Fumi (1951, 1952*a*, *b*, *c*) has derived the schemes for all crystal classes, using the 'direct inspection' method; Murnaghan (1951) and Krishnamurty (1952) have considered isotropic materials and have given identical schemes, containing three independent coefficients for these materials.

The objects of the present paper are to clarify some points connected with the definition of the third-order coefficients; to discuss some of the properties of the relevant sixth-order tensor; to give a systematic derivation of the schemes of coefficients for all crystal classes and for isotropic materials, using the principle of invariance of strain energy; and to discuss briefly one physical application of the third-order coefficients.

2. Definitions; and properties of the tensors

As given by equation (2), the contribution of the third-order coefficients to the strain energy is

$$\varphi_3 = c_{ijklmn}\eta_{ij}\eta_{kl}\eta_{mn}\,, \quad (3)$$

where i, j, k, l, m, n may take any of the values 1, 2, 3, and where the summation convention is implied so that repetition of a suffix means summation with respect to that suffix. Birch (1947), however, writes:

$$\varphi_3 = \Sigma C_{pqr}\eta_p\eta_q\eta_r\,, \quad (4)$$

where $p \leqslant q \leqslant r$, and the summation convention is not implied; p, q, and r may take any of the values 1, 2, 3, 4, 5 and 6, and the relations between the η_p and the η_{ij} are simply

$$\eta_1=\eta_{11};\ \eta_2=\eta_{22};\ \eta_3=\eta_{33};\ \eta_4=\eta_{23};\ \eta_5=\eta_{13};\ \eta_6=\eta_{12}. \quad (5)$$

It should be particularly noted that the change from the double-suffix to the single-suffix notation represented by equations (5) is frequently accompanied by the introduction of the factor 2 into those equations for which $i \neq j$. For instance, the equations in the I.R.E. Standard (1949) are

$$S_1 = S_{11};\ S_2 = S_{22};\ S_3 = S_{33};\ S_4 = 2S_{23};\ S_5 = 2S_{13};\ S_6 = 2S_{12},$$

where S denotes an infinitesimal strain component, but this convention is not followed in equations (5) and the η_p are therefore true tensor components.

The full expansion of equation (4) is given by Birch,* and the complete list of coefficients C_{pqr} is given in column 1, Table 3, where, for convenience, only the suffixes are listed.

The first four terms of equation (4) are

$$\varphi_3=C_{111}\eta_1^3+C_{112}\eta_1^2\eta_2+C_{113}\eta_1^2\eta_3+C_{114}\eta_1^2\eta_4+\ldots. \quad (6)$$

In view of the summation convention, there are thirteen terms of equation (3) which correspond to the above four; taking into account equations (5), and the relations

$$C_{pqr} = C_{rpq} = C_{qrp} \text{ etc.},$$
$$\eta_{ij} = \eta_{ji},$$

these terms reduce to

$$\varphi_3 = c_{111111}\eta_1^3+3c_{111122}\eta_1^2\eta_2 +3c_{111133}\eta_1^2\eta_3+6c_{111123}\eta_1^2\eta_4+\ldots, \quad (7)$$

and, comparing equations (6) and (7),

$$C_{111} = c_{111111};\ C_{112} = 3c_{111122};\ C_{113} = 3c_{111133};\ C_{114} = 6c_{111123}. \quad (8)$$

Proceeding in this way, the ratio

$$R = C_{pqr}/c_{ijklmn}$$

can be found, and the values of R for all C_{pqr} are given in column 1, Table 5.

The application of the strain energy method to the enumeration of the independent second-order coefficients c_{ijkl} in all crystal classes is described by Love (1927), and it has been applied to the third-order coefficients of cubic crystals by Birch (1947). In the remainder of the present paper, this method will be used for a systematic enumeration of the independent third-order coefficients in all crystal classes, and in the isotropic system.

It is convenient to describe the method and to present the results in three sections, the first dealing with the monoclinic, orthorhombic, tetragonal and cubic systems, the second with the trigonal and hexagonal systems, and the third with the isotropic system. Birch's notation is followed, so that the third-order constants referred to subsequently are defined by equation (4). To avoid the excessive use of suffixes, the letter C is omitted from Tables 3 and 5; an entry 111, for example, stands for C_{111} and an entry 3.111−112 for $3C_{111}-C_{112}$.

* The term $C_{566}\eta_5\eta_6^2$ is missing from Birch's equation.

3. Method and results: monoclinic, orthorhombic, tetragonal and cubic systems

The method is described in principle by Birch (1947) and applied by him in detail to the cubic system, but for completeness, an account of it is given here.

The invariance of the strain energy with respect to transformation of axes is expressed by

$$C_{111}\eta_1^3+C_{112}\eta_1^2\eta_2+\ldots = C'_{111}(\eta'_1)^3+C'_{112}(\eta'_1)^2\eta'_2+\ldots.$$

If the transformation is one corresponding with the symmetry of the crystal (i.e. if it is a covering operation) then $C'_{111} = C_{111}$, $C'_{112} = C_{112}$ etc. and

$$C_{111}\eta_1^3+C_{112}\eta_1^2\eta_2+\ldots = C_{111}(\eta'_1)^3+C_{112}(\eta'_1)^2\eta'_2+\ldots. \quad (9)$$

The co-ordinates x_1, x_2 and x_3 transform according to the equations: $x'_j = a_{ij}x_i$, or in full:

$$\left.\begin{aligned} x'_1 &= a_{11}x_1+a_{21}x_2+a_{31}x_3,\\ x'_2 &= a_{12}x_1+a_{22}x_2+a_{32}x_3,\\ x'_3 &= a_{13}x_1+a_{23}x_2+a_{33}x_3, \end{aligned}\right\} \quad (10)$$

where the a_{ij} are the direction cosines. The strains transform according to the equations:

$$\eta'_{kl} = a_{ik}a_{jl}\eta_{ij}, \quad (11)$$

where $i, j, k, l = 1, 2$ or 3. The usual convention is observed in equations (11) whereby repetition of a suffix implies summation with respect to that suffix.

The transformations required for present purposes, and the associated direction cosines, are listed in Table 1.

The symbols at the head of the columns in Table 1 are based on the Hermann–Mauguin notation (Phillips, 1946), and correspond with the following elements of symmetry: $\bar{1}$ = centre; $2(x_1)$ = rotation through 180° about x_1; $2(x_2)$ = rotation through 180° about x_2; $2(x_3)$ = rotation through 180° about x_3; $m(x_1)$ = reflexion in plane perpendicular to x_1; $m(x_2)$ = reflexion in plane perpendicular to x_2; $m(x_3)$ = reflexion in plane perpendicular to x_3; 4 = rotation through 90° about x_3; $\bar{4}$ = rotation through 90° about x_3, followed by inversion through a centre at the origin (Phillips, 1946).

The direction cosines in Table 1, when inserted in equations (11), lead to the strain components in

Table 1. *Transformations and direction cosines*

Symbol	$\bar{1}$	$2(x_1)$	$2(x_2)$	$2(x_3)$	$m(x_1)$	$m(x_2)$	$m(x_3)$	4	$\bar{4}$
$a_{11} =$	−1	1	−1	−1	−1	1	1	0	0
$a_{12} =$	0	0	0	0	0	0	0	−1	1
$a_{21} =$	0	0	0	0	0	0	0	1	−1
$a_{22} =$	−1	−1	1	−1	1	−1	1	0	0
$a_{33} =$	−1	−1	−1	1	1	1	−1	1	−1

$$a_{13} = a_{23} = a_{31} = a_{32} = 0$$

Table 2. *Strain components*

Symbol	$\bar{1}$	$2(x_1)$	$2(x_2)$	$2(x_3)$	$m(x_1)$	$m(x_2)$	$m(x_3)$	4	$\bar{4}$
$\eta_1' =$	η_1	η_1	η_1	η_1	η_1	η_1	η_1	η_2	η_2
$\eta_2' =$	η_2	η_2	η_2	η_2	η_2	η_2	η_2	η_1	η_1
$\eta_3' =$	η_3	η_3	η_3	η_3	η_3	η_3	η_3	η_3	η_3
$\eta_4' =$	η_4	η_4	$-\eta_4$	$-\eta_4$	η_4	$-\eta_4$	$-\eta_4$	$-\eta_5$	$-\eta_5$
$\eta_5' =$	η_5	$-\eta_5$	η_5	$-\eta_5$	$-\eta_5$	η_5	$-\eta_5$	η_4	η_4
$\eta_6' =$	η_6	$-\eta_6$	$-\eta_6$	η_6	$-\eta_6$	$-\eta_6$	η_6	$-\eta_6$	$-\eta_6$

Table 2. Finally, these strain components are put into equation (9), a procedure which leads to the vanishing of some of the coefficients C_{pqr} for all operations except $\bar{1}$ and to equalities among some coefficients for the operations 4 and $\bar{4}$.

Thus, in the case of a four-fold axis, equation (9) becomes:

$$\begin{aligned} &C_{111}\eta_1^3+C_{112}\eta_1^2\eta_2+\ldots+C_{114}\eta_1^2\eta_4+\ldots C_{122}\eta_1\eta_2^2+\ldots \\ &\quad+C_{222}\eta_2^3+\ldots+C_{225}\eta_2^2\eta_5+\ldots \\ &\quad= C_{111}\eta_2^3+C_{112}\eta_1\eta_2^2+\ldots-C_{114}\eta_2^2\eta_5+\ldots+C_{122}\eta_1^2\eta_2 \\ &\quad+\ldots+C_{222}\eta_1^3+\ldots+C_{225}\eta_1^2\eta_4+\ldots, \end{aligned}$$

and by equating coefficients of like products of strains, we obtain:

$$\begin{aligned} &C_{111} = C_{222};\ C_{112} = C_{122}; \\ &\qquad C_{114} = C_{225} = -C_{225}\ (\text{i.e. } C_{114} = C_{225} = 0)\,. \end{aligned}$$

Proceeding in this way the complete scheme of coefficients can be derived; the results are given in Table 3, in which the letter C is omitted, so that the entries give the suffixes of the coefficients only. The entry in any space has to be equated to the one on the same line in column 1. Thus, for example, in the tetragonal system, $C_{111} = C_{111}$ (i.e. C_{111} is independent) and $C_{114} = 0$. The column headings, reading from top to bottom are: (1) name of system, (2) the Hermann–Mauguin and the Schönflies symbols of the classes (Phillips, 1946), (3) notes if any, (4) the number of independent coefficients and (5) column number.

The three columns under 'Monoclinic' correspond with different choices of principal axis. It is now recommended (I.R.E., 1949) that x_2 should be regarded as the principal axis in the monoclinic system, but in the older literature the principal axis was often taken as x_3, and the schemes of coefficients for both choices of principal axis are accordingly included in Table 3. These schemes, and the one corresponding to the choice of x_1 as principal axis, are also required in the derivation of some of the results to be given later. The scheme for the orthorhombic system (column 5) is obtained by combining the results for any two perpendicular two-fold axes or of any two perpendicular mirror planes (columns 2, 3 and 4). The scheme for the sub-division of the tetragonal system (column 7) is obtained by combining the results for a four-fold axis along x_3 (column 6) with those for a mirror plane coinciding with x_1x_3 or x_2x_3 or with those for a two-fold axis along x_1 or x_2 (columns 2 and 3).

Following Birch (1947), the schemes for the cubic system are derived as follows:

(*a*) *Classes* 23, $2/m\,\bar{3}$.—The cubic axes are two-fold and the coefficients are accordingly found by imposing on the scheme for the orthorhombic system (column 5) the transformation

$$x_1 \to x_2;\ x_2 \to x_3;\ x_3 \to x_1\,.$$

This transformation expresses the invariance of properties with respect to cyclic interchange of cubic axes, and corresponds with the existence of trigonal axes along the cube diagonals. It leads to the relations among the non-zero orthorhombic coefficients:

$$\begin{aligned} &C_{111} = C_{222} = C_{333};\ C_{112} = C_{133} = C_{223}; \\ &C_{113} = C_{122} = C_{233};\ C_{144} = C_{255} = C_{366}; \\ &C_{166} = C_{244} = C_{355};\ C_{155} = C_{266} = C_{344}; \\ &C_{123} = C_{123};\ C_{456} = C_{456}\,, \end{aligned}$$

leaving a total of eight independent coefficients which are set out in column 8, Table 3.

(*b*) *Classes* $\bar{4}3\,m$, 432, $4/m\,\bar{3}\,2/m$.—The derivation is similar to that just discussed but the existence of four-fold cubic axes leads to the additional relations:

$$C_{112} = C_{113};\ C_{155} = C_{166}\,,$$

leaving six independent coefficients which are set out in column 9, Table 3. The numbers of independent coefficients in all columns of Table 3 agree with those obtained by Bhagavantam & Suryanarayana (1947,

Table 3.

Triclinic	Monoclinic			Orthorhombic	Tetragonal		Cubic	
$1 (C_1)$ $\bar{1} (S_2)$	$2 (C_2)$ $m (C_s)$ $\frac{2}{m} (C_{2h})$			$222 (V)$ $2mm (C_{2v})$ $\frac{2}{m}\frac{2}{m}\frac{2}{m} (V_h)$	$4 (C_4)$ $\bar{4} (S_4)$ $\frac{4}{m} (C_{4h})$	$4mm (C_{4v})$ $\bar{4}2m (V_d)$ $422 (D_4)$ $\frac{4}{m}\frac{2}{m}\frac{2}{m} (D_{4h})$	$23 (T)$ $\frac{2}{m}\bar{3} (T_h)$	$\bar{4}3m (T_d)$ $432 (O)$ $\frac{4}{m}\bar{3}\frac{2}{m} (O_h)$
	Mirror plane = x_2x_3 Twofold axis = x_1	Mirror plane = x_1x_3 Twofold axis = x_2	Mirror plane = x_1x_2 Twofold axis = x_3					
56 (1)	32 (2)	32 (3)	32 (4)	20 (5)	16 (6)	12 (7)	8 (8)	6 (9)
111	111	111	111	111	111	111	111	111
112	112	112	112	112	112	112	112	112
113	113	113	113	113	113	113	113	112
114	114	0	0	0	0	0	0	0
115	0	115	0	0	0	0	0	0
116	0	0	116	0	116	0	0	0
122	122	122	122	122	112	112	113	112
123	123	123	123	123	123	123	123	123
124	124	0	0	0	0	0	0	0
125	0	125	0	0	0	0	0	0
126	0	0	126	0	0	0	0	0
133	133	133	133	133	133	133	112	112
134	134	0	0	0	0	0	0	0
135	0	135	0	0	0	0	0	0
136	0	0	136	0	136	0	0	0
144	144	144	144	144	144	144	144	144
145	0	0	145	0	145	0	0	0
146	0	146	0	0	0	0	0	0
155	155	155	155	155	155	155	155	155
156	156	0	0	0	0	0	0	0
166	166	166	166	166	166	166	166	155
222	222	222	222	222	111	111	111	111
223	223	223	223	223	113	113	112	112
224	224	0	0	0	0	0	0	0
225	0	225	0	0	0	0	0	0
226	0	0	226	0	-116	0	0	0
233	233	233	233	233	133	133	113	112
234	234	0	0	0	0	0	0	0
235	0	235	0	0	0	0	0	0
236	0	0	236	0	-136	0	0	0
244	244	244	244	244	155	155	166	155
245	0	0	245	0	-145	0	0	0
246	0	246	0	0	0	0	0	0
255	255	255	255	255	144	144	144	144
256	256	0	0	0	0	0	0	0
266	266	266	266	266	166	166	155	155
333	333	333	333	333	333	333	111	111
334	334	0	0	0	0	0	0	0
335	0	335	0	0	0	0	0	0
336	0	0	336	0	0	0	0	0
344	344	344	344	344	344	344	155	156
345	0	0	345	0	0	0	0	0
346	0	346	0	0	0	0	0	0
355	355	355	355	355	344	344	166	155
356	356	0	0	0	0	0	0	0
366	366	366	366	366	366	366	144	144
444	444	0	0	0	0	0	0	0
445	0	445	0	0	0	0	0	0
446	0	0	446	0	446	0	0	0
455	455	0	0	0	0	0	0	0
456	456	456	456	456	456	456	456	456
466	466	0	0	0	0	0	0	0
555	0	555	0	0	0	0	0	0
556	0	0	556	0	-446	0	0	0
566	0	566	0	0	0	0	0	0
666	0	0	666	0	0	0	0	0

1949) and Jahn (1949); the actual schemes also agree with those derived by Fumi (1951).

4. Method and results: trigonal and hexagonal systems

In order to deal with the trigonal, hexagonal and isotropic systems it is necessary to consider a general rotation about the x_3 axis through an angle θ. In this case, the direction cosines in equations (10) become, for a pure rotation,

$$a_{11} = m,\ a_{21} = n,\ a_{31} = 0\,,$$
$$a_{12} = -n,\ a_{22} = m,\ a_{32} = 0\,,$$
$$a_{13} = 0,\ a_{23} = 0,\ a_{33} = 1\,,$$

where $m = \cos\theta$, $n = \sin\theta$. Substitution of these direction cosines into equations (11) leads to the known transformation equations for the strain components:

$$\left.\begin{aligned}
\eta_1' &= m^2\eta_1+n^2\eta_2+2mn\eta_6\,,\\
\eta_2' &= n^2\eta_1+m^2\eta_2-2mn\eta_6\,,\\
\eta_3' &= \eta_3\,,\\
\eta_4' &= m\eta_4-n\eta_5\,,\\
\eta_5' &= n\eta_4+m\eta_5\,,\\
\eta_6' &= -mn\eta_1+mn\eta_2+(m^2-n^2)\eta_6\,.
\end{aligned}\right\} \tag{12}$$

Further substitution of equations (12) in equation (9) leads to the systems of equations ($A1$–$A10$) (see also Appendix).

The values of $a_{11}\ldots a_{33}$ for trigonal and hexagonal axes are set out in Table 4.

Table 4. *Values of* $a_{11}\ldots a_{33}$

Axis	3	$\bar{3}$	6	$\bar{6}$
$a_{11}=$	$-\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	$-\frac{1}{2}$
$a_{21}=$	$\frac{1}{2}\sqrt{3}$	$-\frac{1}{2}\sqrt{3}$	$\frac{1}{2}\sqrt{3}$	$-\frac{1}{2}\sqrt{3}$
$a_{12}=$	$-\frac{1}{2}\sqrt{3}$	$\frac{1}{2}\sqrt{3}$	$-\frac{1}{2}\sqrt{3}$	$\frac{1}{2}\sqrt{3}$
$a_{22}=$	$-\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	$-\frac{1}{2}$
$a_{33}=$	1	-1	1	-1

$$a_{13}=a_{23}=a_{31}=a_{32}=0$$

Equations (A1)

	C'_{111}	C'_{112}	C'_{116}	C'_{122}	C'_{126}	C'_{166}	C'_{222}	C'_{226}	C'_{266}	C'_{666}
$C_{111}=$	m^6	m^4n^2	$-m^5n$	m^2n^4	$-m^3n^3$	m^4n^2	n^6	$-mn^5$	m^2n^4	$-m^3n^3$
$C_{112}=$	$3m^4n^2$	$m^6+2m^2n^4$	$m^5n-2m^3n^3$	$2m^4n^2+n^6$	$m^3n^3-m^5n-mn^5$	$m^2n^4-2m^4n^2$	$3m^2n^4$	$mn^5-2m^3n^3$	$m^4n^2-2m^2n^4$	$3m^3n^3$
$C_{116}=$	$6m^5n$	$4m^3n^3-2m^5n$	$m^6-5m^4n^2$	$2mn^5-4m^3n^3$	$3m^4n^2-3m^2n^4$	$4m^3n^3-2m^5n$	$-6mn^5$	$5m^2n^4-n^6$	$2mn^5-4m^3n^3$	$3m^4n^2-3m^2n^4$
$C_{122}=$	$3m^2n^4$	$2m^4n^2+n^6$	$2m^3n^3-mn^5$	$2m^2n^4+m^6$	$m^5n+mn^5-m^3n^3$	$m^4n^2-2m^2n^4$	$3m^4n^2$	$2m^3n^3-m^5n$	$m^2n^4-2m^4n^2$	$-3m^3n^3$
$C_{126}=$	$12m^3n^3$	$4m^5n-4m^3n^3+4mn^5$	$6m^4n^2-6m^2n^4$	$4m^3n^3-4mn^5-4m^5n$	$m^6-5m^4n^2+5m^2n^4-n^6$	$2m^5n+2mn^5-8m^3n^3$	$-12m^3n^3$	$6m^4n^2-6m^2n^4$	$8m^3n^3-2m^5n-2mn^5$	$6m^2n^4-6m^4n^2$
$C_{166}=$	$12m^4n^2$	$4m^2n^4-8m^4n^2$	$4m^5n-8m^3n^3$	$4m^4n^2-8m^2n^4$	$8m^3n^3-2m^5n-2mn^5$	$m^6+5m^2n^4-6m^4n^2$	$12m^2n^4$	$4mn^5-8m^3n^3$	$5m^4n^2-6m^2n^4+n^6$	$6m^3n^3-3m^5n-3mn^5$
$C_{222}=$	n^6	m^2n^4	mn^5	m^4n^2	m^3n^3	m^2n^4	m^6	m^5n	m^4n^2	m^3n^3
$C_{226}=$	$6mn^5$	$4m^3n^3-2mn^5$	$5m^2n^4-n^6$	$2m^5n-4m^3n^3$	$3m^4n^2-3m^2n^4$	$4m^3n^3-2mn^5$	$-6m^5n$	$m^6-5m^4n^2$	$2m^5n-4m^3n^3$	$3m^4n^2-3m^2n^4$
$C_{266}=$	$12m^2n^4$	$4m^4n^2-8m^2n^4$	$8m^3n^3-4mn^5$	$4m^2n^4-8m^4n^2$	$2mn^5-8m^3n^3+2m^5n$	$5m^4n^2-6m^2n^4+n^6$	$12m^4n^2$	$8m^3n^3-4m^5n$	$m^6-6m^4n^2+5m^2n^4$	$3m^5n-6m^3n^3+3mn^5$
$C_{666}=$	$8m^3n^3$	$-8m^3n^3$	$4m^4n^2-4m^2n^4$	$8m^3n^3$	$4m^2n^4-4m^4n^2$	$2m^5n-4m^3n^3+2mn^5$	$-8m^3n^3$	$4m^4n^2-4m^2n^4$	$4m^3n^3-2m^5n-2mn^5$	$m^6-3m^4n^2+3m^2n^4-n^6$

Equations (A2)

	C'_{114}	C'_{115}	C'_{124}	C'_{125}	C'_{146}	C'_{156}	C'_{224}	C'_{225}	C'_{246}	C'_{256}	C'_{466}	C'_{566}
$C_{114}=$	m^5	m^4n	m^3n^2	m^2n^3	$-m^4n$	$-m^3n^2$	mn^4	n^5	$-m^2n^3$	$-mn^4$	m^3n^2	m^2n^3
$C_{115}=$	$-m^4n$	m^5	$-m^2n^3$	m^3n^2	m^3n^2	$-m^4n$	$-n^5$	mn^4	mn^4	$-m^2n^3$	$-m^2n^3$	m^3n^2
$C_{124}=$	$2m^3n^2$	$2m^2n^3$	m^5+mn^4	m^4n+n^5	$m^4n-m^2n^3$	$m^3n^2-mn^4$	$2m^3n^2$	$2m^2n^3$	$m^2n^3-m^4n$	$mn^4-m^3n^2$	$-2m^3n^2$	$-2m^2n^3$
$C_{125}=$	$-2m^2n^3$	$2m^3n^2$	$-m^4n-n^5$	m^5+mn^4	$mn^4-m^3n^2$	$m^4n-m^2n^3$	$-2m^2n^3$	$2m^3n^2$	$m^3n^2-mn^4$	$m^2n^3-m^4n$	$2m^2n^3$	$-2m^3n^2$
$C_{146}=$	$4m^4n$	$4m^3n^2$	$2m^2n^3-2m^4n$	$2mn^4-2m^3n^2$	$m^5-3m^3n^2$	$m^4n-3m^2n^3$	$-4m^2n^3$	$-4mn^4$	$3m^3n^2-mn^4$	$3m^2n^3-n^5$	$2m^2n^3-2m^4n$	$2mn^4-2m^3n^2$
$C_{156}=$	$-4m^3n^2$	$4m^4n$	$2m^3n^2-2mn^4$	$2m^2n^3-2m^4n$	$3m^2n^3-m^4n$	$m^5-3m^3n^2$	$4mn^4$	$-4m^2n^3$	$n^5-3m^2n^3$	$3m^3n^2-mn^4$	$2m^3n^2-2mn^4$	$2m^2n^3-2m^4n$
$C_{224}=$	mn^4	n^5	m^3n^2	m^2n^3	m^2n^3	mn^4	m^5	m^4n	m^4n	m^3n^2	m^3n^2	m^2n^3
$C_{225}=$	$-n^5$	mn^4	$-m^2n^3$	m^3n^2	$-mn^4$	m^2n^3	$-m^4n$	m^5	$-m^3n^2$	m^4n	$-m^2n^3$	m^3n^2
$C_{246}=$	$4m^2n^3$	$4mn^4$	$2m^4n-2m^2n^3$	$2m^3n^2-2mn^4$	$3m^3n^2-mn^4$	$3m^2n^3-n^5$	$-4m^4n$	$-4m^3n^2$	$m^5-3m^3n^2$	$m^4n-3m^2n^3$	$2m^4n-2m^2n^3$	$2m^3n^2-2mn^4$
$C_{256}=$	$-4mn^4$	$4m^2n^3$	$2mn^4-2m^3n^2$	$2m^4n-2m^2n^3$	$n^5-3m^2n^3$	$3m^3n^2-mn^4$	$4m^3n^2$	$-4m^4n$	$3m^2n^3-m^4n$	$m^5-3m^3n^2$	$2mn^4-2m^3n^2$	$2m^4n-2m^2n^3$
$C_{466}=$	$4m^3n^2$	$4m^2n^3$	$-4m^3n^2$	$-4m^2n^3$	$2m^4n-2m^2n^3$	$2m^3n^2-2mn^4$	$4m^3n^2$	$4m^2n^3$	$2m^2n^3-2m^4n$	$2mn^4-2m^3n^2$	$m^5-2m^3n^2+mn^4$	$m^4n-2m^2n^3+n^5$
$C_{566}=$	$-4m^2n^3$	$4m^3n^2$	$4m^2n^3$	$-4m^3n^2$	$2mn^4-2m^3n^2$	$2m^4n-2m^2n^3$	$-4m^2n^3$	$4m^3n^2$	$2m^3n^2-2mn^4$	$2m^2n^3-2m^4n$	$2m^2n^3-m^4n-n^5$	$m^5-2m^3n^2+mn^4$

Equations (A3)

	C'_{113}	C'_{123}	C'_{136}	C'_{223}	C'_{236}	C'_{366}
$C_{113}=$	m^4	m^2n^2	$-m^3n$	n^4	$-mn^3$	m^2n^2
$C_{123}=$	$2m^2n^2$	m^4+n^4	m^3n-mn^3	$2m^2n^2$	mn^3-m^3n	$-2m^2n^2$
$C_{136}=$	$4m^3n$	$2mn^3-2m^3n$	$m^4-3m^2n^2$	$-4mn^3$	$3m^2n^2-n^4$	$2mn^3-2m^3n$
$C_{223}=$	n^4	m^2n^2	mn^3	m^4	m^3n	m^2n^2
$C_{236}=$	$4mn^3$	$2m^3n-2mn^3$	$3m^2n^2-n^4$	$-4m^3n$	$m^4-3m^2n^2$	$2m^3n-2mn^3$
$C_{366}=$	$4m^2n^2$	$-4m^2n^2$	$2m^3n-2mn^3$	$4m^2n^2$	$2mn^3-2m^3n$	$m^4-2m^2n^2+n^4$

Equations (A4)

	C'_{134}	C'_{135}	C'_{234}	C'_{235}	C'_{346}	C'_{356}
$C_{134}=$	m^3	m^2n	mn^2	n^3	$-m^2n$	$-mn^2$
$C_{135}=$	$-m^2n$	m^3	$-n^3$	mn^2	mn^2	$-m^2n$
$C_{234}=$	mn^2	n^3	m^3	m^2n	m^2n	mn^2
$C_{235}=$	$-n^3$	mn^2	$-m^2n$	m^3	$-mn^2$	m^2n
$C_{346}=$	$2m^2n$	$2mn^2$	$-2m^2n$	$-2mn^2$	m^3-mn^2	m^2n-n^3
$C_{356}=$	$-2mn^2$	$2m^2n$	$2mn^2$	$-2m^2n$	n^3-m^2n	m^3-mn^2

Equations (A5)

	C'_{144}	C'_{145}	C'_{155}	C'_{244}	C'_{245}	C'_{255}	C'_{446}	C'_{456}	C'_{556}
$C_{144}=$	m^4	m^3n	m^2n^2	m^2n^2	mn^3	n^4	$-m^3n$	$-m^2n^2$	$-mn^3$
$C_{145}=$	$-2m^3n$	$m^4-m^2n^2$	$2m^3n$	$-2mn^3$	$m^2n^2-n^4$	$2mn^3$	$2m^2n^2$	mn^3-m^3n	$-2m^2n^2$
$C_{155}=$	m^2n^2	$-m^3n$	m^4	n^4	$-mn^3$	m^2n^2	$-mn^3$	m^2n^2	$-m^3n$
$C_{244}=$	m^2n^2	mn^3	n^4	m^4	m^3n	m^2n^2	m^3n	m^2n^2	mn^3
$C_{245}=$	$-2mn^3$	$m^2n^2-n^4$	$2mn^3$	$-2m^3n$	$m^4-m^2n^2$	$2m^3n$	$-2m^2n^2$	m^3n-mn^3	$2m^2n^2$
$C_{255}=$	n^4	$-mn^3$	m^2n^2	m^2n^2	$-m^3n$	m^4	mn^3	$-m^2n^2$	m^3n
$C_{446}=$	$2m^3n$	$2m^2n^2$	$2mn^3$	$-2m^3n$	$-2m^2n^2$	$-2mn^3$	$m^4-m^2n^2$	m^3n-mn^3	$m^2n^2-n^4$
$C_{456}=$	$-4m^2n^2$	$2m^3n-2mn^3$	$4m^2n^2$	$4m^2n^2$	$2mn^3-2m^3n$	$-4m^2n^2$	$2mn^3-2m^3n$	$m^4-2m^2n^2+n^4$	$2m^3n-2mn^3$
$C_{556}=$	$2mn^3$	$-2m^2n^2$	$2m^3n$	$-2mn^3$	$2m^2n^2$	$-2m^3n$	$m^2n^2-n^4$	mn^3-m^3n	$m^4-m^2n^2$

Equations (A6)

$$C_{133} = m^2C'_{133}+n^2C'_{233}-mnC'_{336}$$
$$C_{233} = n^2C'_{133}+m^2C'_{233}+mnC'_{336}$$
$$C_{336} = 2mnC'_{133}-2mnC'_{233}+(m^2-n^2)C'_{336}$$

Equations (A7)

$$C_{344} = m^2C'_{344}+mnC'_{345}+n^2C'_{355}$$
$$C_{345} = -2mnC'_{344}+(m^2-n^2)C'_{345}+2mnC'_{355}$$
$$C_{355} = n^2C'_{344}-mnC'_{345}+m^2C'_{355}$$

Equations (A8)

$$C_{444} = m^3C'_{444}+m^2nC'_{445}+mn^2C'_{455}+n^3C'_{555}$$
$$C_{445} = -3m^2nC'_{444}+(m^3-2mn^2)C'_{445}+(2m^2n-n^3)C'_{455}+3mn^2C'_{555}$$
$$C_{455} = 3mn^2C'_{444}+(n^3-2m^2n)C'_{445}+(m^3-2mn^2)C'_{455}+3m^2nC'_{555}$$
$$C_{555} = -n^3C'_{444}+mn^2C'_{445}-m^2nC'_{455}+m^3C'_{555}$$

Equations (A9)

$$C_{334} = mC'_{334}+nC'_{335}$$
$$C_{335} = -nC'_{334}+mC'_{335}$$

Equation (A10)

$$C_{333} = C'_{333}$$

The direction cosines for $\bar{3}$ in Table 4 correspond to a rotation through 120°, followed by inversion through a centre at the origin, and those for $\bar{6}$ to a rotation through 60° followed by inversion through the centre (Phillips, 1946). These direction cosines are obtained simply by reversing the signs of those for the simple axes; it is easy to verify that this change leaves the strain transformation equations (12), and therefore equations ($A1$) to ($A10$), unaltered.

Substitution of the values of m and n from Table 4 into equations ($A1$) to ($A10$) leads to systems of simultaneous equations with numerical coefficients, of which the solutions are given below.

Equations ($A1$): *trigonal and hexagonal systems*

$$C_{122} = 3C_{111}+C_{112}-3C_{222};$$
$$C_{166} = -6C_{111}-C_{112}+9C_{222};$$
$$C_{266} = 6C_{111}-C_{112}-3C_{222};\ C_{126} = -2C_{116};$$
$$C_{226} = C_{116};\ C_{666} = -\tfrac{4}{3}C_{116}.$$

Equations ($A2$): *trigonal system*

$$C_{156} = 2C_{114}+3C_{124};\ C_{224} = -C_{114}-C_{124};$$
$$C_{256} = 2C_{114}-C_{124};\ C_{466} = 2C_{124};$$

$$C_{146} = -2C_{115}-3C_{125};\ C_{225} = -C_{115}-C_{125};$$
$$C_{246} = -2C_{115}+C_{125};\ C_{566} = 2C_{125}.$$

Equations ($A2$): *hexagonal system*

$$C_{114} = C_{115} = C_{124} = C_{125} = C_{146} = C_{156} = C_{224} = C_{225} = C_{246} = C_{256} = C_{466} = C_{566} = 0.$$

Equations ($A3$): *trigonal and hexagonal systems*

$$C_{136} = C_{236} = 0;\ C_{113} = C_{223};\ C_{366} = 2C_{113}-C_{123}.$$

Equations ($A4$): *trigonal system*

$$C_{234} = -C_{134};\ C_{356} = 2C_{134};\ C_{235} = -C_{135};$$
$$C_{346} = -2C_{135}.$$

Equations ($A4$): *hexagonal system*

$$C_{134} = C_{135} = C_{234} = C_{235} = C_{346} = C_{356} = 0.$$

Equations ($A5$): *trigonal and hexagonal systems*

$$C_{145} = -C_{245} = C_{446} = -C_{556};\ C_{144} = C_{255};$$
$$C_{155} = C_{244};\ C_{456} = 2(C_{155}-C_{144}).$$

Equations ($A6$): *trigonal and hexagonal systems*

$$C_{133} = C_{233};\ C_{336} = 0.$$

Equations ($A7$): *trigonal and hexagonal systems*

$$C_{344} = C_{355};\ C_{345} = 0.$$

Equations ($A8$): *trigonal system*

$$C_{455} = -3C_{444};\ C_{555} = -\tfrac{1}{3}C_{445}.$$

Equations ($A8$): *hexagonal system*

$$C_{444} = C_{445} = C_{455} = C_{555} = 0.$$

Equations ($A9$): *hexagonal and trigonal systems*

$$C_{334} = C_{335} = 0.$$

Equation ($A10$): *hexagonal and trigonal systems*

$$C_{333} = C_{333}.$$

The above results are summarized in columns 3 and 5 of Table 5, where, just as in Table 3, the letter C is omitted. Reading from top to bottom, the column headings give: (1) name of system, (2) the Hermann–Mauguin and the equivalent Schönflies symbols (Phillips, 1946), (3) the number of independent coefficients, (4) notes, if any, and (5) column number.

The results for the hexagonal system can alternatively be derived quite simply from the trigonal coefficients by combining the results for a three-fold axis along x_3 (column 3, Table 5) with those for a two-fold axis along x_3 or a mirror plane x_1x_2 (column 4,

Table 5.

	Triclinic	Trigonal		Hexagonal		Isotropic
n	$1 (C_1)$ $\bar{1} (S_2)$	$3 (C_3)$ $\bar{3} (C_{3i})$	$3m (C_{3v})$ $32 (D_3)$ $\bar{3}\frac{2}{m} (D_{3d})$ Mirror plane $= x_2x_3$ Twofold axis $= x_1$	$6 (C_6)$ $\bar{6} (C_{3h})$ $\frac{6}{m} (C_{6h})$	$\bar{6}m2 (D_{3h})$ $6mm (C_{6v})$ $622 (D_6)$ $\frac{6}{m}\frac{2}{m}\frac{2}{m} (D_{6h})$	
	56	20	14	12	10	3
(1)	(2)	(3)	(4)	(5)	(6)	(7)
1	111	111	111	111	111	111
3	112	112	112	112	112	112
3	113	113	113	113	113	112
6	114	114	114	0	0	0
6	115	115	0	0	0	0
6	116	116	0	116	0	0
3	122	3.111+112−3.222	3.111+112−3.222	3.111+112−3.222	3.111+112−3.222	112
6	123	123	123	123	123	123
12	124	124	124	0	0	0
12	125	125	0	0	0	0
12	126	−2.116	0	−2.116	0	0
3	133	133	133	133	133	112
12	134	134	134	0	0	0
12	135	135	0	0	0	0
12	136	0	0	0	0	0
12	144	144	144	144	144	2.112−123
24	145	145	0	145	0	0
24	146	−2.115−3.125	0	0	0	0
12	155	155	155	155	155	3.111−112
24	156	2.114+3.124	2.114+3.124	0	0	0
12	166	−6.111−112+9.222	−6.111−112+9.222	−6.111−112+9.222	−6.111−112+9.222	3.111−112
1	222	222	222	222	222	111
3	223	113	113	113	113	112
6	224	−114−124	−114−124	0	0	0
6	225	−115−125	0	0	0	0
6	226	116	0	116	0	0
3	233	133	133	133	133	112
12	234	−134	−134	0	0	0
12	235	−135	0	0	0	0
12	236	0	0	0	0	0
12	244	155	155	155	155	3.111−112
24	245	−145	0	−145	0	0
24	246	−2.115+125	0	0	0	0
12	255	144	144	144	144	2.112−123
24	256	2.114−124	2.114−124	0	0	0
12	266	6.111−112−3.222	6.111−112−3.222	6.111−112−3.222	6.111−112−3.222	3.111−112
1	333	333	333	333	333	111
6	334	0	0	0	0	0
6	335	0	0	0	0	0
6	336	0	0	0	0	0
12	344	344	344	344	344	3.111−112
24	345	0	0	0	0	0
24	346	−2.135	0	0	0	0
12	355	344	344	344	344	3.111−112
24	356	2.134	2.134	0	0	0
12	366	2.113−123	2.113−123	2.113−123	2.113−123	2.112−123
8	444	444	444	0	0	0
24	445	445	0	0	0	0
24	446	145	0	145	0	0
24	455	−3.444	−3.444	0	0	0
48	456	2.155−2.144	2.155−2.144	2.155−2.144	2.155−2.144	6.111−6.112+2.123
24	466	2.124	2.124	0	0	0
8	555	−445/3	0	0	0	0
24	556	−145	0	−145	0	0
24	566	2.125	0	0	0	0
8	666	−4.116/3	0	−4.116/3	0	0

Table 3); this derivation is related to those discussed by Fumi (1952*a*, *c*). Column 4, Table 5, is derived by combining the results of column 3, Table 5, with those of column 2, Table 3; and column 6, Table 5, by combining column 5, Table 5, either with column 2 or column 3, Table 3.

The schemes of independent coefficients in columns 3–6, Table 5, agree with those given by Fumi (1952*b*), but it is necessary to note that Fumi's table refers to the c_{ijklmn} constants, and in comparing his results with Table 5, the complete set of equations similar to (8) must be taken into account. For example, Fumi gives an equation which in the present notation is:

$$c_{112222} = c_{111111} - c_{222222} + c_{111122}\,; \qquad (13)$$

Now from column 1, Table 5,

$$C_{122} = 3c_{112222}\,;\; C_{111} = c_{111111}\,;$$
$$C_{222} = c_{222222}\,;\; C_{112} = 3c_{111122}\,. \qquad (14)$$

Substituting (14) in (13):

$$\tfrac{1}{3}C_{122} = C_{111}-C_{222}+\tfrac{1}{3}C_{112},$$
$$\text{i.e. } C_{122} = 3C_{111}-3C_{222}+C_{112}\,,$$

in agreement with the entries in Table 5.

5. Isotropic system

Column 7, Table 5, headed 'Isotropic', actually gives the scheme of constants obtained by combining the results for maximum symmetry in the cubic and hexagonal systems (column 9, Table 3 and column 6, Table 5). This scheme contains three independent constants, in agreement with the number predicted by Jahn (1949) and by Venkatarayudu & Krishnamurty (1952); the actual scheme of coefficients also agrees with those given by Murnaghan (1951) and Krishnamurty (1952).

The full form of φ_3 from column 7, Table 5, is:

$$\begin{aligned}\varphi_3 = {} & C_{111}\eta_1^3+C_{112}\eta_1^2\eta_2+C_{112}\eta_1^2\eta_3+C_{112}\eta_1\eta_2^2+C_{123}\eta_1\eta_2\eta_3 \\ & +C_{112}\eta_1\eta_3^2+(2C_{112}-C_{123})\eta_1\eta_4^2+(3C_{111}-C_{112})\eta_1\eta_5^2 \\ & +(3C_{111}-C_{112})\eta_1\eta_6^2+C_{111}\eta_2^3+C_{112}\eta_2^2\eta_3+C_{112}\eta_2\eta_3^2 \\ & +(3C_{111}-C_{112})\eta_2\eta_4^2+(2C_{112}-C_{123})\eta_2\eta_5^2 \\ & +(3C_{111}-C_{112})\eta_2\eta_6^2+C_{111}\eta_3^3+(3C_{111}-C_{112})\eta_3\eta_4^2 \\ & +(3C_{111}-C_{112})\eta_3\eta_5^2+(2C_{112}-C_{123})\eta_3\eta_6^2 \\ & +(6C_{111}-6C_{112}+2C_{123})\eta_4\eta_5\eta_6\,. \qquad (15)\end{aligned}$$

In terms of the invariants of strain (Love, 1927)

$$\begin{aligned}I_1 &= \eta_1+\eta_2+\eta_3\,, \\ I_2 &= \eta_2\eta_3-\eta_4^2+\eta_1\eta_3-\eta_5^2+\eta_1\eta_2-\eta_6^2\,, \\ I_3 &= \eta_1\eta_2\eta_3+2\eta_4\eta_5\eta_6-\eta_1\eta_4^2-\eta_2\eta_5^2-\eta_3\eta_6^2\,,\end{aligned}$$

equation (15) becomes:

$$\varphi_3 = C_{111}(I_1^3+3[I_3-I_1I_2]) +C_{112}(I_1I_2-3I_3)+C_{123}I_3\,. \qquad (16)$$

If the fundamental constants are taken as C_{111}, C_{155} and C_{456}, equation (16) can be written rather more simply as:

$$\varphi_3 = C_{111}I_1^3-C_{155}I_1I_2+\tfrac{1}{2}C_{456}I_3\,. \qquad (17)$$

It is well known (Love, 1927; Murnaghan, 1951) that for terms of the second degree in the strains,

$$\varphi_2 = \tfrac{1}{2}(\lambda+2\mu)I_1^2-2\mu I_2\,, \qquad (18)$$

where λ and μ are the Lamé constants expressible in terms of the usual second-order elastic constants by the equations

$$\lambda+2\mu = c_{11},\ \mu = c_{66} = \tfrac{1}{2}(c_{11}-c_{12})\,. \qquad (19)$$

Thus, when terms of the second and third degree in the strains are taken into account, the strain energy of an isotropic body is, by equations (2), (17), (18) and (19),

$$2\varphi = c_{11}I_1^2-4c_{66}I_2+2C_{111}I_1^3-2C_{155}I_1I_2+C_{456}I_3\,.$$

As mentioned earlier, Kaplan (1931) found that φ_3 contained two coefficients only; in terms of the present notation, the additional relation found by Kaplan is

$$C_{123} = 2C_{112}-3C_{111}\,.$$

Kaplan derived this equation by considering the most general rotation of the axes, i.e. one in which all of the direction cosines in equations (10) differ from zero, but the exact details of the derivation are not clear, and the writer has been unable to verify it. (An attempt to communicate with Dr Kaplan was unsuccessful.)

It does not seem possible, however, for a relation of this type to exist without the introduction of special assumptions such as those discussed by Herpin (1949). Equations (16) and (17), which have now in effect been derived independently by Murnaghan (1951), Krishnamurty (1952) and the writer, show that φ_3 is expressible in terms of three coefficients and of the three strain invariants. By hypothesis, the coefficients of an isotropic solid are invariant for any rotation, and so, of course, are the strain invariants. Thus the imposition of any rotation whatsoever on equations (16) and (17) will simply lead to an identity and there can be no further reduction in the number of independent coefficients.

6. A physical application

Direct application of the concept of third-order elastic coefficients to physical problems is limited by two circumstances, one theoretical in that the algebra becomes very complicated, particularly when applied to crystal systems containing large numbers of coefficients, the other practical in that application of high stresses to crystalline materials usually results in slip along definite planes, a mode of deformation to which the third-order coefficients do not apply.

Birch (1938), however, has minimised the first difficulty by considering isotropic materials, and materials belonging to the cubic group of maximum symmetry (Birch, 1947), and has avoided the second by dealing with an arbitrary homogeneous infinitesimal strain superimposed on a finite hydrostatic strain.

A specific problem solved by Birch (1947) is the effect of hydrostatic pressure on the elastic stiffnesses, c_{ik}, of a material belonging to the cubic group of maximum symmetry and therefore possessing six independent third-order constants. For such a material, Birch derives the equations

$$\left.\begin{aligned}c_{11}' &= c_{11}+\eta(2c_{11}+2c_{12}+6C_{111}+4C_{112})\,, \\ c_{12}' &= c_{12}+\eta(C_{123}+4C_{112}-c_{11}-c_{12})\,, \\ c_{44}' &= c_{44}+\eta(c_{11}+2c_{12}+c_{44}+\tfrac{1}{2}C_{144}+C_{166})\,,\end{aligned}\right\} \qquad (20)$$

where c_{11}, c_{12} and c_{44} are the stiffnesses measured at zero hydrostatic pressure; the primes denote the apparent values of the stiffnesses measured under a

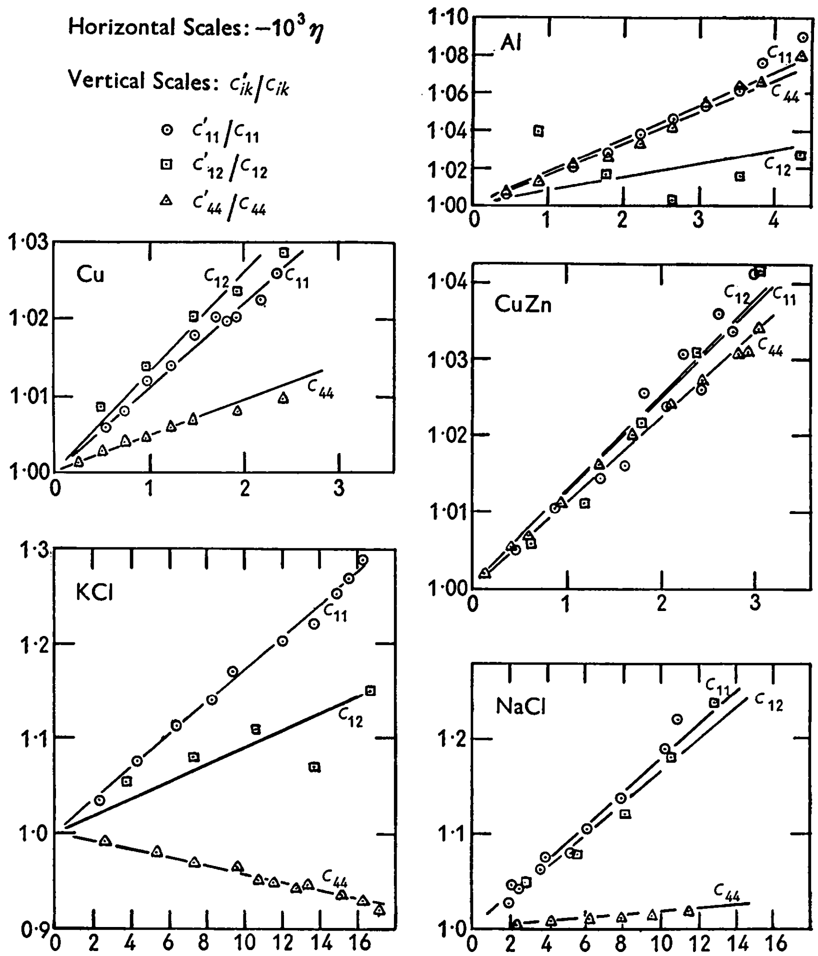

Fig. 1.

hydrostatic pressure P; and η is a quantity defined by the equation

$$V/V_0 = (1+2\eta)^{\frac{3}{2}}, \tag{21}$$

V_0 being the original volume and V the volume when compressed by the pressure P.

The apparent stiffnesses of the cubic crystals KCl, NaCl, CuZn, Cu and Al have been measured by Lazarus (1949) up to hydrostatic pressures of 10,000 bars, using a pulse transmission method. Lazarus plotted the ratio c'_{ik}/c_{ik} against P and obtained straight-line relationships. If, however, equations (20) are correct, the ratio should be a linear function of η. The conversion from P to η is easily accomplished with the aid of equation (21), in conjunction with the equation

$$1-V/V_0 = aP-bP^2,$$

using for the purpose the values of a and b recorded by Lazarus for his five materials.

The resulting graphs are shown in Fig. 1, from which it can be concluded that the use of η in a straight-line relationship with c'_{ik}/c_{ik} is empirically as justifiable as the use of P, and, from a theoretical point of view, the use of η is preferable since it is in accordance with equations (20).

Assuming the correctness of these equations, estimates can be made of the numerical values of the combinations $(6C_{111}+4C_{112})$, $(C_{123}+4C_{112})$ and $(\frac{1}{2}C_{144}+C_{166})$. In fact, denoting these combinations for brevity by C_a, C_b and C_d, it follows from equations (20) that

$$\left.\begin{aligned} C_a &= c_{11}s_a-2(c_{11}+c_{12}), \\ C_b &= c_{12}s_b+c_{11}+c_{12}, \\ C_d &= c_{44}s_d-c_{11}-2c_{12}-c_{44}, \end{aligned}\right\} \tag{22}$$

where

s_a is the slope of the (c'_{11}/c_{11}) *v.* η graph,
s_b is the slope of the (c'_{12}/c_{12}) *v.* η graph,
s_d is the slope of the (c'_{44}/c_{44}) *v.* η graph.

Numerical estimates of s_a, s_b and s_d were obtained from Fig. 1, drawn to a larger scale, and these, when inserted into equations (22), together with the zero pressure stiffnesses measured by Lazarus, yield the values of C_a, C_b and C_d given in Table 6; it is of interest that all of the C's in this table are negative, and are numerically about an order of magnitude larger than the stiffnesses c_{ik}.

Table 6. *Third order constants*

Unit = 10^{11} dyne cm.$^{-2}$

Material	KCl	NaCl	CuZn	Cu	Al
C_a	−81	−100	−208	−249	−225
C_b	− 1·5	− 14	−114	−133	− 32
C_d	− 3·5	− 11	−135	− 84	− 74

The information on the third order constants yielded by the above treatment is unavoidably incomplete in giving effectively only three constants out of a possible six. In addition, the values obtained are probably not highly accurate, since they contain not only the original errors of the experiments, but also the errors associated with reading the values from Lazarus's graphs. It appears, however, that no numerical estimates of the third-order constants have hitherto been published, nor have methods of measuring them been suggested, and the present analysis has been carried out as a first step in remedying these deficiencies.

In principle, solutions for the effect of hydrostatic pressure on stiffnesses could be obtained for materials of any symmetry by appropriate modification of the treatment applied by Birch to cubic materials, but the labour involved in the mathematical development would be considerable, and might be prohibitive for systems of low symmetry.

In the case of isotropic materials, the relations

$$C_{144} = 2C_{112}-C_{123}; \; C_{166} = 3C_{111}-C_{112}; \; c_{44} = \tfrac{1}{2}(c_{11}-c_{12})$$

reduce the three equations (20) to two:

$$c'_{11} = c_{11}+\eta(2c_{11}+2c_{12}+C_a)\,,$$
$$c'_{12} = c_{12}+\eta(C_b-c_{11}-c_{12})\,.$$

Experiments similar to those of Lazarus, if carried out on isotropic materials, would therefore effectively yield two out of the three independent third-order constants, but the data required for these calculations are not at present available.

This paper is published by permission of the Department of Scientific and Industrial Research. Acknowledgment is made of the assistance obtained from correspondence with Prof. S. Bhagavantam, Osmania University, Hyderabad, and especially with Prof. F. G. Fumi, University of Milan. As a result of Prof. Fumi's criticisms, a significant error was discovered in an early draft of this paper.

APPENDIX

Equations ($A1$–$A10$) above are the transformation equations for the third-order coefficients corresponding to a rotation through an angle θ from x_1 towards x_2 about the x_3 axis. The equations are to be read horizontally, e.g.

$$C_{111} = m^6C'_{111}+m^4n^2C'_{112}-m^5nC'_{116}+\ldots\,,$$

where $m = \cos\theta$, $n = \sin\theta$.

References

Bhagavantam, S. & Suryanarayana, D. (1947). *Nature, Lond.* **160**, 750.

Bhagavantam, S. & Suryanarayana, D. (1949). *Acta Cryst.* **2**, 21.

Birch, F. (1938). *J. Appl. Phys.* **9**, 279.

Birch, F. (1947). *Phys. Rev.* **71**, 809.

Fumi, F. G. (1951). *Phys. Rev.* **83**, 1274.

Fumi, F. G. (1952*a*). *Acta Cryst.* **5**, 44.

Fumi, F. G. (1952*b*). *Phys. Rev.* **86**, 561.

Fumi, F. G. (1952*c*). *Acta Cryst.* **5**, 691.

Herpin, A. (1949). *C. R. Acad. Sci., Paris*, **229**, 921.

Institute of Radio Engineers. (1949). *Proc. Inst. Radio Engrs.*, N. Y. **37**, 1378.

Jahn, H. A. (1949). *Acta Cryst.* **2**, 30.

Kaplan, C. (1931). *Phys. Rev.* **38**, 1020.

Krishnamurty, T. S. G. (1952). *Curr. Sci.* **21**, 8.

Lazarus, D. (1949). *Phys. Rev.* **76**, 545.

Love, A. E. H. (1927). *The Mathematical Theory of Elasticity*, 4th ed. Cambridge: University Press.

Murnaghan, F. D. (1951). *Finite Deformation of an Elastic Solid.* New York: Wiley; London: Chapman and Hall.

Phillips, F. C. (1946). *An Introduction to Crystallography.* London: Longmans Green.

Venkatarayudu, T. & Krishnamurty, T. S. G. (1952). *Acta Cryst.* **5**, 287.