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Seed layer formation by deposition of micro-crystallites on a revolving substrate. Part II: application to some nonlinear effects

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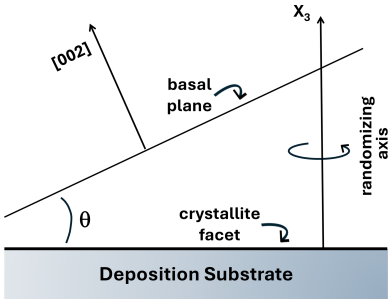
The matrix method of averaging material coefficients of crystallites deposited at an angle to a revolving substrate, disclosed in the prequel [Ballato & Ballato (2024). *Acta Cryst.* B**80**, 760–765], is applied to tensors in their indicial form. The results are used to determine averaged nonlinear dielectric, piezoelectric, and elastic constants, as well as linear pyroelectric coefficients, for triclinic crystals; these are further specialized for Laue classes of higher symmetry.

1. Introduction

In Part I (Ballato & Ballato, 2024), referred to subsequently as (I), a simple model was proposed for averaging material coefficients of crystallites deposited at an angle to a revolving substrate. It was implemented to determine the average linear dielectric permittivity, piezoelectric stress, and elastic stiffness matrices for all Laue classes, as functions of those of an unrotated single crystal. These particular coefficients were selected because they are employed in many electro-elastic applications (Weigel *et al.*, 2002), and serve as examples applied to tensorial rank 2, 3 and 4 effects (Bhagavantam & Suryanarayana, 1949; Smith, 1958; Huntington, 1958; Mason, 1966; Nye, 1985). Here the model is applied to some nonlinear versions of these quantities.

The phenomenology of recoverable electro–elastic interactions in materials in the continuum approximation is often expressed in the form of power series expansions of an energy function, yielding coefficients of various orders (Truesdell & Toupin, 1960). In many instances first-order estimations prove to be admirably sufficient for practical applications. The linear equations of piezo-elasticity are a notable example (Forsbergh, 1956; IEEE Standard on Piezoelectricity, 1987). Increasingly, however, departures from the linear regime have become important (Truesdell & Noll, 1965; Forsbergh, 1956; Gagnepain & Besson, 1975; Maugin, 1986; Hruška, 2014). In discussions of nonlinearities, however, one must distinguish the cases where cause–effect relations are strictly single valued and those that exhibit hysteresis, or history-dependent behavior (Guo *et al.*, 2025). This latter case is briefly mentioned in Section 5.5, where ferroelectric materials and linear pyroelectricity are discussed.



2. Rationale for this work

It has long been recognized that the thin film fabrication scenarios depicted in (I) give rise to strains at the hetero-

structure interfaces (Fujiwara *et al.*, 1986; Nishino, 1989; Jain *et al.*, 1997). Indeed, it is to be expected that any discontinuities in the elastic and electric fields at junctions might require consideration of nonlinearities. Such gradients arise, *e.g.* in superlattices (Wierzbicka *et al.*, 2025), in composites, where two or more sub-materials or phases are joined at the microscopic scale, but are macroscopically homogeneous (van Suchtelen, 1972; van den Boomgaard *et al.*, 1976*a*; van den Boomgaard *et al.*, 1976*b*), and in multiferroics, which are homogeneous on the microscopic scale (Newnham, 2005; Fiebig *et al.*, 2016).

Apart from configurations where macroscopic spatial discontinuities / gradients produce nonlinear effects, atomic-level anharmonicities associated with the Grüneisen equation of state (Grüneisen, 1912; Anderson, 2000) implicitly involve considerations of nonlinearity. Examples include thermal conductivity / heat transport (Casimir, 1938; Kittel, 1949; Iwanowski *et al.*, 2025), and optical nonlinearities (Shanshool *et al.*, 2026). Section 5 provides further particulars.

An additional application of nonlinearities is to computation of temperature coefficients of the elastic stiffnesses. There are two contributions to these anharmonicities: the first is the geometrical nonlinearity, comprised of products of linear thermoelastic coefficients and the linear elastic stiffnesses; this geometrical portion is closely related to Poisson's ratio considerations (Ballato, 2010). The second contribution is the physical nonlinearity, comprised of products of linear thermoelastic coefficients and nonlinear elastic stiffnesses (Lee *et al.*, 1975; Sorokin *et al.*, 1999; Sorokin & Telichko, 2011; Sorokin & Telichko, 2012). Temperature- and stress-insensitive crystal orientations for high-precision frequency control of oscillators have been realized by judicious compensation of elastic nonlinearities (Ballato, 1977).

3. Nonlinear terms identified

Many material tensors (of differing ranks) that characterize various physical interactions are enumerated, *e.g.* in Bhagavantam & Venkatarayudu (1962), Mason (1966), Nye (1985). The efficient matrix method used in (I) is limited to rank 4 and below (Auld, 1973), otherwise the full tensor expansion must be used (Bond, 1943). Three-dimensional tensors will in general have 3^{rank} components, but when indicial symmetries, required by a particular physical effect, are taken into account, the number of independent coefficients is reduced. The same tensor rank may as well correspond to a number of various effects, albeit with differing numbers of components. For example, the rank 4 tensor in Mindlin's polarization gradient theory (Mindlin, 1968) relates six stress or strain variables with nine independent polarization gradients, so the $3^4 = 81$ rank 4 components are reduced in this instance to 54.

We adopt schematic versions of the series expansions of Gagnepain & Besson (1975) given on page 251 of that work, specifically their equations (20) and (21) to identify the terms to be evaluated. Similar expressions are considered by Lv *et al.* (2025). Terminology, symbols, and conventions are as given in (I) and by Ballato & Ballato (2023). For didactic purposes, tensor ranks are indicated by superscripts in parentheses.

Equation (20): $T^{(2)} \propto c^{(4)}S^{(2)} + c^{(6)}[S^{(2)}]^2 + c^{(8)}[S^{(2)}]^3 - e^{(3)}E^{(1)} - e^{(4)}[E^{(1)}]^2 - e^{(5)}E^{(1)}S^{(2)} - e^{(7)}E^{(1)}[S^{(2)}]^2 - e^{(6)}[E^{(1)}]^2S^{(2)} - e^{(5)}[E^{(1)}]^3 + \cdots$. The first and fourth terms were treated in (I).

Equation (21): $D^{(1)} \propto e^{(3)}S^{(2)} + e^{(4)}E^{(1)}S^{(2)} + e^{(5)}[S^{(2)}]^2 + e^{(7)}[S^{(2)}]^3 + e^{(6)}E^{(1)}[S^{(2)}]^2 + \hat{e}^{(5)}[E^{(1)}]^2S^{(2)} + \varepsilon^{(2)}E^{(1)} + \varepsilon^{(3)}[E^{(1)}]^2 + \varepsilon^{(4)}[E^{(1)}]^3 + \cdots$. The first and seventh terms were treated in (I).

The lowest-order nonlinear portions of these equations are: $T^{(2)} \propto + c^{(6)}[S^{(2)}]^2 - e^{(4)}[E^{(1)}]^2 - e^{(5)}E^{(1)}S^{(2)}$ and $D^{(1)} \propto + e^{(4)}E^{(1)}S^{(2)} + e^{(5)}[S^{(2)}]^2 + \varepsilon^{(3)}[E^{(1)}]^2$. The remaining terms represent higher-order (and usually insignificant) nonlinearities, and are disregarded for our purposes. We choose, as representative, the following nonlinearities:

Rank 3: dielectric permittivity tensor $\varepsilon^{(3)}$ from $D^{(1)} \propto + \varepsilon^{(3)}[E^{(1)}]^2$

Rank 4: electrostriction tensor $e^{(4)}$ from $T^{(2)} \propto - e^{(4)}[E^{(1)}]^2$ or $D^{(1)} \propto + e^{(4)}E^{(1)}S^{(2)}$

Rank 5: piezoelectric stress tensor $e^{(5)}$ from $T^{(2)} \propto - e^{(5)}E^{(1)}S^{(2)}$ or $D^{(1)} \propto + e^{(5)}[S^{(2)}]^2$

Rank 6: elastic stiffness tensor $c^{(6)}$ from $T^{(2)} \propto + c^{(6)}[S^{(2)}]^2$

In tensor notation these quantities appear, respectively, as: $\varepsilon^{(3)} \rightarrow \varepsilon_{ij\lambda}$; $e^{(4)} \rightarrow e_{hijk} \rightarrow e_{\lambda\mu}$; $e^{(5)} \rightarrow e_{kghij} \rightarrow e_{k\lambda\mu}$; and $c^{(6)} \rightarrow c_{fghijk} \rightarrow c_{\lambda\mu\nu}$. As usual, Roman indices range 1, 2, 3 and Greek (Voigt) indices range 1, 2, … 6.

The expansions given can also be expressed in the form of reciprocal relations. For example, the nonlinear elastic stiffnesses $c^{(6)}$ have compliance counterparts $s^{(6)}$ determined from the relation $S_{ijklmn} = -S_{ijpq}S_{klrs}S_{mnuv}C_{pqrsuv}$ (Ballato, 2001; Kube & Turner, 2016). Compliances are used to characterize the nonlinear behavior of thin rods and bars (Tiersten & Ballato, 1983).

4. The model

Micro-crystallites are deposited on a revolving substrate. Prior to the deposition, in the reference state the crystallite x_3 axis is taken to be normal to the substrate reference plane; a first rotation is then made about its x_1 or x_2 axis. Upon deposition, a specified facet is taken to lie on the substrate plane. The x_3

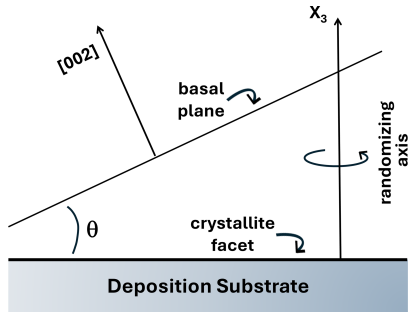


Figure 1
Schematic of the deposition geometry. The crystallite facet lies upon the substrate; its x_3 axis, shown as [002], subtends cone angle θ with respect to the substrate randomizing axis X_3.

axis of the crystallite is thus inclined with respect to the substrate normal (X_3) by a facet angle θ; see Fig. 1.

As a result of the x_1 or x_2 90° rotation, followed by the θ inclination, material coefficients (generically symbolized as q) that originally referred to crystallographic axes (IEEE Standard on Piezoelectricity, 1987) are transformed to new coefficients q'.

Subsequent rotation of the crystallite sitting on the substrate plane is described by a rotation, in angle φ, about the substrate X_3 axis. This creates a distribution of crystallite normals ([002] in the diagram) that form a cone about the substrate normal. A suitable angular averaging then yields average values, applied to the individual tensor components, $\langle q'' \rangle = (1/2\pi) \int_0^{2\pi} q' \mathrm{d}\varphi$, where q' is the quantity to be averaged.

5. Model results ordered by rank and Laue group

In this section are given the averaged components, $\langle'' \rangle$, of the nonlinear coefficients selected above, ordered by rank and Laue group (Bechmann & Hearmon, 1969; Brendel, 1979). Ordering by rank avoids the confusion of terms such as first-order, third-order *etc*.

5.1. Rank 3, nonlinear dielectric permittivities, $\varepsilon^{(3)}$

The nonlinear dielectric permittivity (ε_{ijk}) is a tensor of rank 3, symmetric in the indices assigned to the two independent electric field directions. By converting these two indices into Voigt form, the $3^3 = 27$ components are reduced to 18 in the general Laue group I (triclinic) case. The outcome is isomorphic with the linear piezoelectric effect treated in (I). The averaging results may therefore be recovered from Section 3.2 of (I) for all Laue classes; in Table 5 thereof the coefficient of e_{15} should read C, not C^2.

Under the conditions posited by Kleinman (1962*a*, 1962*b*) for optical second-harmonic generation (SHG), all three indices permute, and the 18 conditions are further reduced to 10, which we take as those with the Voigt indices: 11, 12, 13, 14, 15, 16, 22, 23, 24 and 33. The Kleinman indicial identities are: 21 = 16, 25 = 36 = 14, 26 = 12, 31 = 15, 32 = 24, 34 = 23 and 35 = 13. The hyperpolarizability tensor obeys the same relations; it is a molecular (microscopic) cause, whereas SHG is a collective (macroscopic) and observable effect arising therefrom.

Application of the averaging procedure, outlined in (I) to the SHG tensor yields the triclinic results given in Tables 1 and 2. The seven elements $\langle \varepsilon''_{11} \rangle$, $\langle \varepsilon''_{12} \rangle$, $\langle \varepsilon''_{13} \rangle$, $\langle \varepsilon''_{14} \rangle$, $\langle \varepsilon''_{16} \rangle$, $\langle \varepsilon''_{22} \rangle$ and $\langle \varepsilon''_{23} \rangle$ vanish identically for both x_1 and x_2 rotations, leaving only $\langle \varepsilon''_{15} \rangle$, $\langle \varepsilon''_{24} \rangle$ and $\langle \varepsilon''_{33} \rangle$, but $\langle \varepsilon''_{24} \rangle \equiv \langle \varepsilon''_{15} \rangle$, so there are but two SHG $\langle \varepsilon'' \rangle$ coefficients. Furthermore, the coefficients ε_{11}, ε_{12}, ε_{14} and ε_{13} do not appear in the expressions for $\langle \varepsilon''_{15} \rangle$ and $\langle \varepsilon''_{33} \rangle$.

Twelve point groups have finite SHG $\langle e'' \rangle$ values; these are given in Table 3. Classes 222, 422, 622, $\overline{4}2m$, 32, $\overline{6}m2$, 23 and $\overline{4}3m$ are identically zero when $\langle \varepsilon'' \rangle$ averaging is applied, and the pairs (*m*, *mm*2), (4, 6), (3, 3*m*) and (4*mm*, 6*mm*) have the same form.

Table 1
Rank 3 averaged nonlinear dielectric permittivities for triclinic Laue group I, with first rotation x_1.

Optical second-harmonic generation (SHG) conditions of Kleinman (1962*a*, 1962*b*) apply. *C* and *S* are cos(θ) and sin(θ), respectively, where θ is the facet angle.

$\varepsilon_{i\lambda} \rightarrow$	ε_{16}	ε_{15}	ε_{22}	ε_{24}	ε_{23}	ε_{33}
$2\langle \varepsilon''_{15} \rangle$	$-S$	C	$-C^2S$	$C(C^2 - 2S^2)$	$-S(S^2 - 2C^2)$	CS^2
$\langle \varepsilon''_{33} \rangle$			$-S^3$	$3CS^2$	$-3C^2S$	C^3

Table 2
Rank 3 averaged nonlinear dielectric permittivities for triclinic Laue group I, with first rotation x_2.

Optical SHG conditions of Kleinman (1962*a*, 1962*b*) apply. *C* and *S* are cos(θ) and sin(θ), respectively, where θ is the facet angle.

$\varepsilon_{i\lambda} \rightarrow$	ε_{16}	ε_{15}	ε_{22}	ε_{24}	ε_{23}	ε_{33}
$2\langle \varepsilon''_{15} \rangle$	S	C	C^2S	$C(C^2 - 2S^2)$	$2S(S^2 - 2C^2)$	CS^2
$\langle \varepsilon''_{33} \rangle$			S^3	$3CS^2$	$-3C^2S$	C^3

Table 3
Specialization of averaged SHG nonlinear dielectric permittivities $\langle \varepsilon''_{i\lambda} \rangle$ for all Laue groups having finite entries.

To be used in conjunction with Table 1 (x_1 rotation) and Table 2 (x_2 rotation); only $i\lambda$ indices are tabulated.

Laue group	Point group	$i\lambda$ indices					
I	1	15	16	22	23	24	33
II	2	0	16	22	23	0	0
II, III	*m*, *mm*2	15	0	0	0	24	33
IVa, VIa	4, 6	15	0	0	0	15	33
IVa	$\overline{4}$	15	0	0	0	−15	0
Va, Vb	3, 3*m*	15	−22	22	0	15	33
VIa	$\overline{6}$	0	−22	22	0	0	0
IVb, VIb	4*mm*, 6*mm*	15	0	0	0	15	33

Table 4
Rank 4, averaged, nonlinear piezoelectric stress (electrostriction) coefficient matrix for Laue group I.

The form of this matrix is the same for both x_1 and x_2 rotations, while the differences in the individual elements are given in Tables 5 and 6.

$\langle e''_{11} \rangle$	$\langle e''_{12} \rangle$	$\langle e''_{13} \rangle$	0	0	$\langle e''_{16} \rangle$
$\langle e''_{12} \rangle$	$\langle e''_{11} \rangle$	$\langle e''_{13} \rangle$	0	0	$-\langle e''_{16} \rangle$
$\langle e''_{31} \rangle$	$\langle e''_{31} \rangle$	$\langle e''_{33} \rangle$	0	0	0
0	0	0	$\langle e''_{44} \rangle$	$\langle e''_{45} \rangle$	0
0	0	0	$-\langle e''_{45} \rangle$	$\langle e''_{44} \rangle$	0
$-\langle e''_{16} \rangle$	$\langle e''_{16} \rangle$	0	0	0	$\langle e''_{66} \rangle$

5.2. Rank 4, nonlinear piezoelectric stress (electrostriction) coefficients, $e^{(4)}$

Electrostriction is a tensor of rank 4, relating mechanical deformations to imposition of an electric field. The effect is quadratic in the electric field; the $e^{(4)}$ symbols appearing in the relations $T^{(2)} \propto -e^{(4)}[E^{(1)}]^2$ and $D^{(1)} \propto + e^{(4)}E^{(1)}S^{(2)}$ are identical (Hruška, 1965; Hruška, 2014).

Ferroelectric materials are briefly discussed in Section 5.5. A subset of these (relaxor ferroelectrics) (Cross, 1987) are a notable class that possess very high electrostriction and linear dielectric permittivities, with a variety of energy storage, harvesting and conversion applications.

Table 5
The nine independent, averaged, rank 4 electrostriction coefficients $\langle e''_{\lambda\mu}\rangle$ for Laue group I.

In terms of the 36 unrotated $e_{\lambda\mu}$ values; x_1 rotation; see Table 4. Entries are to be read as: $8\langle e''_{\lambda\mu}\rangle = C^4[\,] + C^3[\,] + C^2[\,] + C[\,] + [\,]$. C and S are cos(θ) and sin(θ), respectively, where θ is the facet angle.

$8\langle e''_{11}\rangle =$	$C^4[3e_{22}]$	$C^3[6S(e_{24}+e_{42})]$ $C[2S(e_{14}+e_{41})+4S(e_{56}+e_{65})+6S^3(e_{34}+e_{43})]$	$C^2[(e_{12}+e_{21})+4e_{66}+3S^2(e_{23}+e_{32})+12S^2e_{44}]$ $[3e_{11}+S^2(e_{13}+e_{31})+3S^4e_{33}+4S^2e_{55}]$
$8\langle e''_{12}\rangle =$	$C^4[e_{22}]$	$C^3[2S(e_{24}+e_{42})]$ $C[6S(e_{14}+e_{41})-4S(e_{56}+e_{65})+2S^3(e_{34}+e_{43})]$	$C^2[3(e_{12}+e_{21})-4e_{66}+S^2(e_{23}+e_{32})+4S^2e_{44}]$ $[e_{11}+3S^2(e_{13}+e_{31})+S^4e_{33}-4S^2e_{55}]$
$8\langle e''_{13}\rangle =$	$C^4[4e_{23}]$	$C^3[8S(e_{43}-e_{24})]$ $C[8S^3(e_{42}-e_{34})-8Se_{14}]$	$C^2[4e_{13}+4S^2(e_{22}+e_{33})-16S^2e_{44}]$ $[4S^4e_{32}+4S^2e_{12}]$
$8\langle e''_{16}\rangle =$	$C^4[0]$	$C^3[2(e_{62}-e_{26})]$ $C[2(e_{16}-e_{61})+2S^2(e_{63}-e_{36})+4S^2(e_{54}-e_{45})]$	$C^2[2S(e_{52}-e_{25})+4S(e_{64}-e_{46})]$ $[2S(e_{15}-e_{51})+2S^3(e_{53}-e_{35})]$
$8\langle e''_{31}\rangle =$	$C^4[4e_{32}]$	$C^3[8S(e_{34}-e_{42})]$ $C[8S^3(e_{24}-e_{43})-8S\,e_{41}]$	$C^2[4e_{31}+4S^2(e_{22}+e_{33})-16S^2e_{44}]$ $[4S^4e_{23}+4S^2e_{21}]$
$8\langle e''_{33}\rangle =$	$C^4[8e_{33}]$	$-C^3[16S(e_{34}+e_{43})]$ $-C[16S^3(e_{24}+e_{42})]$	$C^2[8S^2(e_{23}+e_{32})+32S^2e_{44}]$ $[8S^4e_{22}]$
$8\langle e''_{44}\rangle =$	$C^4[4e_{44}]$	$C^3[4S(e_{34}+e_{43})-4S(e_{24}+e_{42})]$ $C[4S^3(e_{24}+e_{42})-4S(e_{65}+e_{56})-4S^3(e_{34}+e_{43})]$	$C^2[4e_{55}+4S^2(e_{22}+e_{33})-4S^2(e_{23}+e_{32})-8S^2e_{44}]$ $[4S^4\,e_{44}+4S^2e_{66}]$
$8\langle e''_{45}\rangle =$	$C^4[0]$	$C^3[4(e_{45}-e_{54})]$ $C[4S^2(e_{26}-e_{62})+4S^2(e_{63}-e_{36})+4S^2(e_{54}-e_{45})]$	$C^2[4S(e_{52}-e_{25})+4S(e_{35}-e_{53})+4S(e_{64}-e_{46})]$ $[4S^3(e_{46}-e_{64})]$
$8\langle e''_{66}\rangle =$	$C^4[e_{22}]$	$C^3[2S(e_{24}+e_{42})]$ $C[4S(e_{56}+e_{65})-2S(e_{41}+e_{14})+2S^3(e_{34}+e_{43})]$	$C^2[4e_{66}-(e_{21}+e_{12})+S^2(e_{23}+e_{32})+4S^2e_{44}]$ $[e_{11}-S^2(e_{13}+e_{31})+S^4e_{33}+4S^2e_{55}]$

Table 6
The nine independent, averaged, rank 4 electrostriction coefficients $\langle e''_{\lambda\mu}\rangle$ for Laue group I.

In terms of the 36 unrotated $e_{\lambda\mu}$ values; x_2 rotation; see Table 4. Entries are to be read as: $8\langle e''_{\lambda\mu}\rangle = C^4[\,] + C^3[\,] + C^2[\,] + C[\,] + [\,]$. C and S are cos(θ) and sin(θ), respectively, where θ is the facet angle.

$8\langle e''_{11}\rangle =$	$C^4[3e_{11}]$	$-C^3[6S(e_{15}+e_{51})]$ $-C[2S(e_{25}+e_{52})+4S(e_{46}+e_{64})+6S^3(e_{35}+e_{53})]$	$C^2[(e_{12}+e_{21})+4e_{66}+3S^2(e_{13}+e_{31})+12S^2e_{55}]$ $[3e_{22}+S^2(e_{23}+e_{32})+3S^4e_{33}+4S^2e_{44}]$
$8\langle e''_{12}\rangle =$	$C^4[e_{11}]$	$-C^3[2S(e_{15}+e_{51})]$ $-C[6S(e_{25}+e_{52})-4S(e_{46}+e_{64})+2S^3(e_{35}+e_{53})]$	$C^2[3(e_{12}+e_{21})-4e_{66}+S^2(e_{13}+e_{31})+4S^2e_{55}]$ $[e_{22}+3S^2(e_{23}+e_{32})+S^4e_{33}-4S^2e_{44}]$
$8\langle e''_{13}\rangle =$	$C^4[e_{13}]$	$-C^3[8S(e_{53}-e_{15})]$ $-C[8S^3(e_{51}-e_{35})-8S\,e_{25}]$	$C^2[4e_{23}+4S^2(e_{11}+e_{33})-16S^2e_{55}]$ $[4S^4e_{31}+4S^2e_{21}]$
$8\langle e''_{16}\rangle =$	$C^4[0]$	$C^3[2(e_{16}-e_{61})]$ $C[2(e_{62}-e_{26})+2S^2(e_{36}-e_{63})+4S^2(e_{54}-e_{45})]$	$C^2[2S(e_{41}-e_{14})+4S(e_{65}-e_{56})]$ $[2S(e_{24}-e_{42})+2S^3(e_{43}-e_{34})]$
$8\langle e''_{31}\rangle =$	$C^4[4e_{31}]$	$-C^3[8S(e_{35}-e_{51})]$ $-C[8S^3(e_{15}-e_{53})-8Se_{52}]$	$C^2[4e_{32}+4S^2(e_{11}+e_{33})-16S^2e_{55}]$ $[4S^4\,e_{13}+4S^2\,e_{12}]$
$8\langle e''_{33}\rangle =$	$C^4[8e_{33}]$	$+C^3[16S(e_{35}+e_{53})]$ $+C[16S^3(e_{15}+e_{51})]$	$C^2[8S^2(e_{13}+e_{31})+32S^2e_{55}]$ $[8S^4e_{11}]$
$8\langle e''_{44}\rangle =$	$C^4[4e_{55}]$	$C^3[4S(e_{15}+e_{51})-4S(e_{35}+e_{53})]$ $C[4S^3(e_{35}+e_{53})+4S(e_{46}+e_{64})-4S^3(e_{15}+e_{51})]$	$C^2[4e_{44}+4S^2(e_{11}+e_{33})-4S^2(e_{13}+e_{31})-8S^2e_{55}]$ $[4S^4e_{55}+4S^2e_{66}]$
$8\langle e''_{45}\rangle =$	$C^4[0]$	$C^3[4(e_{45}-e_{54})]$ $C[4S^2(e_{61}-e_{16})+4S^2(e_{36}-e_{63})+4S^2(e_{54}-e_{45})]$	$C^2[4S(e_{41}-e_{14})+4S(e_{34}-e_{43})+4S(e_{65}-e_{56})]$ $[4S^3(e_{56}-e_{65})]$
$8\langle e''_{66}\rangle =$	$C^4[e_{11}]$	$-C^3[2S(e_{15}+e_{51})]$ $-C[4S(e_{46}+e_{64})-2S(e_{25}+e_{52})+2S^3(e_{35}+e_{53})]$	$C^2[4e_{66}-(e_{21}+e_{12})+S^2(e_{13}+e_{31})+4S^2e_{55}]$ $[e_{22}-S^2(e_{23}+e_{32})+S^4e_{33}+4S^2e_{44}]$

Considering the relation $T^{(2)} \propto -e^{(4)}[E^{(1)}]^2$, the stress tensor is symmetric: $T_{jk} = T_{kj}$, and the electric field products are indistinguishable: $E_mE_n = E_nE_m$; however the stress and electric field indices cannot be reversed; $\lambda\mu \neq \mu\lambda$. Therefore the $3^4 = 81$, rank 4, $e^{(4)}$ components are reduced to 36 for triclinic symmetry, and not to 21 as in the elastic case when Voigt indices are used. When the averaging procedure is applied thereto, for either x_1 or x_2 rotation, the resulting

Table 7
Matrices associated with the expansions of the $\langle e''_{k\lambda\mu}\rangle$ for triclinic Laue group I, x_1 rotation.

This table is used in conjunction with Tables 8, 9 and 10; see text for details. For each of the nine $\langle e''_{3\lambda\mu}\rangle$, all $e_{1\lambda\mu}$ components vanish for the x_1 rotation. Apart from the multiplier, the $e_{2\lambda\mu}$ and $e_{3\lambda\mu}$ entries, for the x_1 rotation, are identical for all 25 of the $\langle e''_{1\lambda\mu}\rangle$, $\langle e''_{2\lambda\mu}\rangle$ and $\langle e''_{3\lambda\mu}\rangle$.

x_1 rotation	$\langle e''_{114}\rangle$	$\langle e''_{115}\rangle$	$\langle e''_{124}\rangle$	$\langle e''_{125}\rangle$	$\langle e''_{134}\rangle$	$\langle e''_{135}\rangle$	$\langle e''_{146}\rangle$	$\langle e''_{156}\rangle$
$e_{1\lambda\mu}$	A	B	C	D	E	F	G	H
$e_{2\lambda\mu}$ and $e_{3\lambda\mu}$	D	C	B	A	F	E	H	G

	$\langle e''_{214}\rangle$	$\langle e''_{215}\rangle$	$\langle e''_{224}\rangle$	$\langle e''_{225}\rangle$	$\langle e''_{234}\rangle$	$\langle e''_{235}\rangle$	$\langle e''_{246}\rangle$	$\langle e''_{256}\rangle$
$e_{1\lambda\mu}$	D	C	B	A	F	E	H	G
$e_{2\lambda\mu}$ and $e_{3\lambda\mu}$	A	B	C	D	E	F	G	H

	$\langle e''_{311}\rangle$	$\langle e''_{312}\rangle$	$\langle e''_{313}\rangle$	$\langle e''_{322}\rangle$	$\langle e''_{323}\rangle$	$\langle e''_{333}\rangle$	$\langle e''_{344}\rangle$	$\langle e''_{355}\rangle$	$\langle e''_{366}\rangle$
$e_{1\lambda\mu}$					Zero				
$e_{2\lambda\mu}$ and $e_{3\lambda\mu}$	I	J	K	I	K	N	P	P	Q

Table 8
Multipliers for the expansions of the $\langle e''_{k\lambda\mu}\rangle$ for triclinic Laue group I, x_1 rotation.

See text for details. Subscript f is the field direction.

$M_f\backslash\langle e''_{1\lambda\mu}\rangle$	$\langle e''_{114}\rangle$	$\langle e''_{115}\rangle$	$\langle e''_{124}\rangle$	$\langle e''_{125}\rangle$	$\langle e''_{134}\rangle$	$\langle e''_{135}\rangle$	$\langle e''_{146}\rangle$	$\langle e''_{156}\rangle$
M_1	1/8	1/8	1/8	1/8	1/2	1/2	1/8	1/8
M_2	$-C/8$	$C/8$	$-C/8$	$C/8$	$-C/2$	$C/2$	$C/8$	$-C/8$
M_3	$-S/8$	$S/8$	$-S/8$	$S/8$	$-S/2$	$S/2$	$S/8$	$-S/8$

$M_f\backslash\langle e''_{2\lambda\mu}\rangle$	$\langle e''_{214}\rangle$	$\langle e''_{215}\rangle$	$\langle e''_{224}\rangle$	$\langle e''_{225}\rangle$	$\langle e''_{234}\rangle$	$\langle e''_{235}\rangle$	$\langle e''_{246}\rangle$	$\langle e''_{256}\rangle$
M_1	1/8	$-1/8$	1/8	$-1/8$	1/2	$-1/2$	$-1/8$	1/8
M_2	$C/8$	$C/8$	$C/8$	$C/8$	$C/2$	$C/2$	$C/8$	$C/8$
M_3	$S/8$	$S/8$	$S/8$	$S/8$	$S/2$	$S/2$	$S/8$	$S/8$

$M_f\backslash\langle e''_{3\lambda\mu}\rangle$	$\langle e''_{311}\rangle$	$\langle e''_{312}\rangle$	$\langle e''_{313}\rangle$	$\langle e''_{322}\rangle$	$\langle e''_{323}\rangle$	$\langle e''_{333}\rangle$	$\langle e''_{344}\rangle$	$\langle e''_{355}\rangle$	$\langle e''_{366}\rangle$
M_1					Zero				
M_2	$-S/8$	$-S/8$	$-S/2$	$-S/8$	$-S/2$	$-S$	$-S/2$	$-S/2$	$-S/8$
M_3	$C/8$	$C/8$	$C/2$	$C/8$	$C/2$	C	$C/2$	$C/2$	$C/8$

triclinic $\langle\varepsilon''\rangle$ contains 18 components, nine of which are independent; these are given in Table 4. It is similar in structure, but not identical, with the tetragonal electrostrictive matrix in Table 6 of Forsbergh (1956). Table 5, for the x_1 rotation, expresses the $\langle e''_{\lambda\mu}\rangle$ in terms of the 36 unrotated $e^{(4)}$ coefficients. The corresponding results for the x_2 rotation are given in Table 6.

When, in Table 5, it is further assumed that $\lambda\mu = \mu\lambda$, the coefficients $\langle e''_{16}\rangle = -\langle e''_{26}\rangle = -\langle e''_{61}\rangle = -\langle e''_{62}\rangle$ and $\langle e''_{45}\rangle = -\langle e''_{54}\rangle$ vanish. Additionally, $\langle e''_{31}\rangle = \langle e''_{13}\rangle$. The resulting relations are those of the averaged linear elastic stiffnesses expressed in an alternative but equivalent form from those in Tables 7, 8, and 9 of (I).

5.3. Rank 5, nonlinear piezoelectric stress moduli $e^{(5)}$

The rank 5 electroelastic effect, mentioned in Section 3 and discussed here, links the stress tensor with the product of electric field and strain tensors; reciprocally, it also links electric displacement with the product of the strain tensors. However, rank 5 phenomena encompass a wide variety of other physical effects including: stress dependence of the bulk photovoltaic effect (Nadupalli *et al.*, 2019), acoustical activity (Portigal & Burstein, 1968; Mindlin & Toupin, 1971; Frenzel *et al.*, 2019), cubic magneto-optic Kerr effect (Gaerner *et al.*, 2024) and altermagnetism (Krempaský *et al.*, 2024). Each of these disparate effects will require consideration of their individual point-group tensors; the commonality, for our purposes, is that they are all of rank 5.

Table 9
Expansions of the matrices A to H in terms of the unrotated $e_{f\lambda\mu}$.

Subscript f is the field direction. C and S stand for $\cos(\theta)$ and $\sin(\theta)$, respectively, where θ is the facet angle.

	A	B	C	D	E	F	G	H
e_{f11}	0	0	0	0	0	0	0	0
e_{f12}	$-3CS$	0	$-CS$	0	0	0	0	CS
e_{f13}	$3CS$	0	CS	0	0	0	0	$-CS$
e_{f14}	$3(C^2-S^2)$	0	(C^2-S^2)	0	0	0	0	$-(C^2-S^2)$
e_{f15}	0	$3C$	0	C	0	0	C	0
e_{f16}	0	$-3S$	0	$-S$	0	0	$-S$	0
e_{f22}	$-(C^3S)$	0	$-(3C^3S)$	0	$-CS^3$	0	0	$-C^3S$
e_{f23}	$CS(C^2-S^2)$	0	$3CS(C^2-S^2)$	0	$-CS(C^2-S^2)$	0	0	$CS(C^2-S^2)$
e_{f24}	$C^2(C^2-3S^2)$	0	$3C^2(C^2-3S^2)$	0	$S^2(3C^2-S^2)$	0	0	$C^2(C^2-3S^2)$
e_{f25}	0	$C(C^2-2S^2)$	0	$C(3C^2+2S^2)$	0	CS^2	$-C(C^2+2S^2)$	0
e_{f26}	0	$-3C^2S$	0	$-C^2S$	0	$-S^3$	$-C^2S$	0
e_{f33}	CS^3	0	$3CS^3$	0	C^3S	0	0	CS^3
e_{f34}	$-S^2(S^2-3C^2)$	0	$-3S^2(S^2-3C^2)$	0	$-C^2(3S^2-C^2)$	0	0	$-S^2(S^2-3C^2)$
e_{f35}	0	$3CS^2$	0	CS^2	0	C^3	CS^2	0
e_{f36}	0	$-S(S^2-2C^2)$	0	$-S(3S^2+2C^2)$	0	$-C^2S$	$S(S^2+2C^2)$	0
e_{f44}	$2CS(C^2-S^2)$	0	$6CS(C^2-S^2)$	0	$-2CS(C^2-S^2)$	0	0	$2CS(C^2-S^2)$
e_{f45}	0	$2S(2C^2-S^2)$	0	$2S(2C^2+S^2)$	0	$-2C^2S$	$-2S^3$	0
e_{f46}	0	$-2C(2S^2-C^2)$	0	$-2C(2S^2+C^2)$	0	$2CS^2$	$2C^3$	0
e_{f55}	$-2CS$	0	$2CS$	0	0	0	0	$2CS$
e_{f56}	$-2(C^2-S^2)$	0	$2(C^2-S^2)$	0	0	0	0	$2(C^2-S^2)$
e_{f66}	$2CS$	0	$-2CS$	0	0	0	0	$-2CS$

Whereas the coefficient arrays for many material relationships depend solely on the Laue group (*e.g.* the linear and nonlinear elastic coefficients), the rank 5 arrays are different for each of the 21 permissible noncentrosymmetric (acentric) point groups, and all are listed in the admirable paper of Grimmer (2007). (Halasyamani & Poeppelmeier, 1998) provide a generous sampling of noncentrosymmetric (acentric) oxide representatives.

It is to be noted that IRE Standards on Piezoelectric Crystals (1949), Bechmann, (1953), Nelson & Hearmon (1979), Ballato & Ballato (2020) use $e_{f\lambda}$ for the linear piezoelectric stress coefficient, and $d_{f\lambda}$ for the linear piezoelectric strain coefficient; hence the corresponding nonlinear coefficients are denoted $e_{f\lambda\mu}$ and $d_{f\lambda\mu}$, respectively; (Grimmer, 2007) reverses these.

5.3.1. Triclinic, Laue I, class 1

Whereas the number of rank 5 terms involves $3^5 = 243$ coefficients in general, elastic symmetries reduce these to 63 coefficients for Laue class I (three field directions times 21 elastic indices). When averaging is applied, only 25 survive; these are identical for both x_1 and x_2 rotations, and are: $\langle e''_{114}\rangle$, $\langle e''_{115}\rangle$, $\langle e''_{124}\rangle$, $\langle e''_{125}\rangle$, $\langle e''_{134}\rangle$, $\langle e''_{135}\rangle$, $\langle e''_{146}\rangle$, $\langle e''_{156}\rangle$, $\langle e''_{214}\rangle$, $\langle e''_{215}\rangle$, $\langle e''_{224}\rangle$, $\langle e''_{225}\rangle$, $\langle e''_{234}\rangle$, $\langle e''_{235}\rangle$, $\langle e''_{246}\rangle$, $\langle e''_{256}\rangle$, $\langle e''_{311}\rangle$, $\langle e''_{312}\rangle$, $\langle e''_{313}\rangle$, $\langle e''_{322}\rangle$, $\langle e''_{323}\rangle$, $\langle e''_{333}\rangle$, $\langle e''_{344}\rangle$, $\langle e''_{355}\rangle$ and $\langle e''_{366}\rangle$. The number of these 25 surviving triclinic $\langle e''\rangle$ coefficients will be further reduced depending on the additional symmetries pertaining to a particular effect.

The full expansion of each of the 25 surviving $\langle e''\rangle$ coefficients will involve, in general, 63 terms for each rotation. As these are somewhat cumbersome, the full expansion for the triclinic case has been organized in the form of four tables for each rotation: for the x_1 rotation, Tables 7, 8, 9 and 10, and for the x_2 rotation, Tables 11, 12, 13 and 14. These are to be read in the generic form: $\langle e''\rangle = M_1Z_1 + M_2Z_2 + M_3Z_3$. The multipliers M_k are given in Tables 8 and 12; the quantities Z_k are found schematically in Tables 7 and 11, and written out in columns in Tables 9, 10, 13 and 14 in terms of the symbols C and S, which, in turn, stand for $\cos(\theta)$ and $\sin(\theta)$, where θ is the facet angle.

Table 10
Expansions of the matrices I to Q in terms of the unrotated $e_{f\lambda\mu}$.

Subscript f is the field direction. C and S stand for $\cos(\theta)$ and $\sin(\theta)$, respectively, where θ is the facet angle.

	I	J	K	N	P	Q
e_{f11}	3	1	0	0	0	1
e_{f12}	$2C^2$	$6C^2$	S^2	0	0	$-2C^2$
e_{f13}	$2S^2$	$6S^2$	C^2	0	0	$-2S^2$
e_{f14}	$4CS$	$12CS$	$-2CS$	0	0	$-4CS$
e_{f15}	0	0	0	0	0	0
e_{f16}	0	0	0	0	0	0
e_{f22}	$3C^4$	C^4	C^2S^2	S^4	C^2S^2	C^4
e_{f23}	$6C^2S^2$	$2C^2S^2$	$C^4 + S^4$	$2C^2S^2$	$-2C^2S^2$	$2C^2S^2$
e_{f24}	$12C^3S$	$4C^3S$	$-2CS(C^2 - S^2)$	$-4CS^3$	$-2CS(C^2 - S^2)$	$4C^3S$
e_{f25}	0	0	0	0	0	0
e_{f26}	0	0	0	0	0	0
e_{f33}	$3S^4$	S^4	C^2S^2	C^4	C^2S^2	S^4
e_{f34}	$12CS^3$	$4CS^3$	$2CS(C^2 - S^2)$	$-4C^3S$	$2CS(C^2 - S^2)$	$4CS^3$
e_{f35}	0	0	0	0	0	0
e_{f36}	0	0	0	0	0	0
e_{f44}	$12C^2S^2$	$4C^2S^2$	$-4C^2S^2$	$4C^2S^2$	$(C^2 - S^2)^2$	$4C^2S^2$
e_{f45}	0	0	0	0	0	0
e_{f46}	0	0	0	0	0	0
e_{f55}	$4S^2$	$-4S^2$	0	0	C^2	$4S^2$
e_{f56}	$8CS$	$-8CS$	0	0	$-2CS$	$8CS$
e_{f66}	$4C^2$	$-4C^2$	0	0	S^2	$4C^2$

Table 11
Matrices associated with the expansions of the $\langle e''_{k\lambda\mu}\rangle$ for triclinic Laue group I, x_2 rotation.

This table is used in conjunction with Tables 12, 13 and 14; see text for details. For each of the nine $\langle e''_{3\lambda\mu}\rangle$, all $e_{2\lambda\mu}$ components vanish for the x_2 rotation. Apart from the multiplier, the $e_{1\lambda\mu}$ and $e_{3\lambda\mu}$ entries, for the x_2 rotation, are identical for all 25 of the $\langle e''_{1\lambda\mu}\rangle$, $\langle e''_{2\lambda\mu}\rangle$ and $\langle e''_{3\lambda\mu}\rangle$.

x_2 rotation	$\langle e''_{114}\rangle$	$\langle e''_{115}\rangle$	$\langle e''_{124}\rangle$	$\langle e''_{125}\rangle$	$\langle e''_{134}\rangle$	$\langle e''_{135}\rangle$	$\langle e''_{146}\rangle$	$\langle e''_{156}\rangle$
$e_{1\lambda\mu}$ and $e_{3\lambda\mu}$	d	c	b	a	f	e	h	g
$e_{2\lambda\mu}$	a	b	c	d	e	f	g	h

	$\langle e''_{214}\rangle$	$\langle e''_{215}\rangle$	$\langle e''_{224}\rangle$	$\langle e''_{225}\rangle$	$\langle e''_{234}\rangle$	$\langle e''_{235}\rangle$	$\langle e''_{246}\rangle$	$\langle e''_{256}\rangle$
$e_{1\lambda\mu}$ and $e_{3\lambda\mu}$	a	b	c	d	e	f	g	h
$e_{2\lambda\mu}$	d	c	b	a	f	e	h	g

	$\langle e''_{311}\rangle$	$\langle e''_{312}\rangle$	$\langle e''_{313}\rangle$	$\langle e''_{322}\rangle$	$\langle e''_{323}\rangle$	$\langle e''_{333}\rangle$	$\langle e''_{344}\rangle$	$\langle e''_{355}\rangle$	$\langle e''_{366}\rangle$
$e_{1\lambda\mu}$ and $e_{3\lambda\mu}$	i	j	k	i	k	n	p	p	q
$e_{2\lambda\mu}$					Zero				

Table 12
Multipliers for the expansions of the $\langle e''_{k\lambda\mu}\rangle$ for triclinic Laue group I, x_2 rotation.

See text for details. Subscript f is the field direction.

$M_f\backslash\langle e''_{1\lambda\mu}\rangle$	$\langle e''_{114}\rangle$	$\langle e''_{115}\rangle$	$\langle e''_{124}\rangle$	$\langle e''_{125}\rangle$	$\langle e''_{134}\rangle$	$\langle e''_{135}\rangle$	$\langle e''_{146}\rangle$	$\langle e''_{156}\rangle$
M_1	$C/8$	$C/8$	$C/8$	$C/8$	$C/2$	$C/2$	$-C/8$	$C/8$
M_2	$-1/8$	$1/8$	$-1/8$	$1/8$	$-1/2$	$1/2$	$1/8$	$1/8$
M_2	$-S/8$	$-S/8$	$-S/8$	$-S/8$	$-S/2$	$-S/2$	$S/8$	$-S/8$

$M_f\backslash\langle e''_{2\lambda\mu}\rangle$	$\langle e''_{214}\rangle$	$\langle e''_{215}\rangle$	$\langle e''_{224}\rangle$	$\langle e''_{225}\rangle$	$\langle e''_{234}\rangle$	$\langle e''_{235}\rangle$	$\langle e''_{246}\rangle$	$\langle e''_{256}\rangle$
M_1	$C/8$	$-C/8$	$C/8$	$-C/8$	$C/2$	$-C/2$	$-C/8$	$-C/8$
M_2	$1/8$	$1/8$	$1/8$	$1/8$	$1/2$	$1/2$	$-1/8$	$1/8$
M_3	$-S/8$	$S/8$	$-S/8$	$S/8$	$-S/2$	$S/2$	$S/8$	$S/8$

$M_f\backslash\langle e''_{3\lambda\mu}\rangle$	$\langle e''_{311}\rangle$	$\langle e''_{312}\rangle$	$\langle e''_{313}\rangle$	$\langle e''_{322}\rangle$	$\langle e''_{323}\rangle$	$\langle e''_{333}\rangle$	$\langle e''_{344}\rangle$	$\langle e''_{355}\rangle$	$\langle e''_{366}\rangle$
M_1	$S/8$	$S/8$	$S/2$	$S/8$	$S/2$	S	$S/2$	$S/2$	$S/8$
M_2					Zero				
M_3	$C/8$	$C/8$	$C/2$	$C/8$	$C/2$	C	$C/2$	$C/2$	$C/8$

Table 13
Expansions of the matrices a to h in terms of the unrotated $e_{f\lambda\mu}$.

Subscript f is the field direction. C and S stand for cos(θ) and sin(θ), respectively, where θ is the facet angle.

	a	b	c	d	e	f	g	h
e_{f11}	C^3S	0	$3C^3S$	0	CS^3	0	0	$-C^3S$
e_{f12}	$3CS$	0	CS	0	0	0	0	CS
e_{f13}	$-CS(C^2-S^2)$	0	$-CS(C^2-S^2)$	0	$CS(C^2-S^2)$	0	0	$CS(C^2-S^2)$
e_{f14}	0	$C(C^2-2S^2)$	0	$C(3C^2+2S^2)$	0	CS^2	$-C(C^2+2S^2)$	0
e_{f15}	$C^2(C^2-3S^2)$	0	$3C^2(C^2-3S^2)$	0	$-S^2(S^2-3C^2)$	0	0	$-C^2(C^2-3S^2)$
e_{f16}	0	$3C^2S$	0	C^2S	0	S^3	C^2S	0
e_{f22}	0	0	0	0	0	0	0	0
e_{f23}	$-3CS$	0	$-CS$	0	0	0	0	$-CS$
e_{f24}	0	$3C$	0	C	0	0	C	0
e_{f25}	$3(C^2-S^2)$	0	(C^2-S^2)	0	0	0	0	(C^2-S^2)
e_{f26}	0	$3S$	0	S	0	0	S	0
e_{f33}	$-CS^3$	0	$-3CS^3$	0	$-C^3S$	0	0	CS^3
e_{f34}	0	$3CS^2$	0	CS^2	0	C^3	CS^2	0
e_{f35}	$-S^2(S^2-3C^2)$	0	$-3S^2(S^2-3C^2)$	0	$C^2(C^2-3S^2)$	0	0	$S^2(S^2-3C^2)$
e_{f36}	0	$S(S^2-2C^2)$	0	$S(3S^2+2C^2)$	0	C^2S	$-S(S^2+2C^2)$	0
e_{f44}	$2CS$	0	$-2CS$	0	0	0	0	$2CS$
e_{f45}	0	$2S(S^2-2C^2)$	0	$-2S(S^2+2C^2)$	0	$2C^2S$	$2S^3$	0
e_{f46}	$-2(C^2-S^2)$	0	$2(C^2-S^2)$	0	0	0	0	$-2(C^2-S^2)$
e_{f55}	$-2CS(C^2-S^2)$	0	$-6CS(C^2-S^2)$	0	$2CS(C^2-S^2)$	0	0	$2CS(C^2-S^2)$
e_{f56}	0	$2C(C^2-2S^2)$	0	$-2C(C^2+2S^2)$	0	$2CS^2$	$2C^3$	0
e_{f66}	$-2CS$	0	$2CS$	0	0	0	0	$-2CS$

Table 14
Expansions of the matrices i to q in terms of the unrotated $e_{f\lambda\mu}$.

Subscript f is the field direction. C and S stand for cos(θ) and sin(θ), respectively, where θ is the facet angle.

	i	j	k	n	p	q
e_{f11}	$3C^4$	C^4	C^2S^2	S^4	C^2S^2	C^4
e_{f12}	$2C^2$	$6C^2$	S^2	0	0	$-2C^2$
e_{f13}	$6C^2S^2$	$2C^2S^2$	(C^4+S^4)	$2C^2S^2$	$-2C^2S^2$	$2C^2S^2$
e_{f14}	0	0	0	0	0	0
e_{f15}	$-12C^3S$	$-4C^3S$	$2CS(C^2-S^2)$	$4CS^3$	$2CS(C^2-S^2)$	$-4C^3S$
e_{f16}	0	0	0	0	0	0
e_{f22}	3	1	0	0	0	1
e_{f23}	$2S^2$	$6S^2$	C^2	0	0	$-2S^2$
e_{f24}	0	0	0	0	0	0
e_{f25}	$-4CS$	$-12CS$	$2CS$	0	0	$4CS$
e_{f26}	0	0	0	0	0	0
e_{f33}	$3S^4$	S^4	C^2S^2	C^4	C^2S^2	S^4
e_{f34}	0	0	0	0	0	0
e_{f35}	$-12CS^3$	$-4CS^3$	$-2CS(C^2-S^2)$	$4C^3S$	$-2CS(C^2-S^2)$	$-4CS^3$
e_{f36}	0	0	0	0	0	0
e_{f44}	$4S^2$	$-4S^2$	0	0	C^2	$4S^2$
e_{f45}	0	0	0	0	0	0
e_{f46}	$-8CS$	$8CS$	0	0	$2CS$	$-8CS$
e_{f55}	$12C^2S^2$	$4C^2S^2$	$-4C^2S^2$	$4C^2S^2$	$(C^2-S^2)^2$	$4C^2S^2$
e_{f56}	0	0	0	0	0	0
e_{f66}	$4C^2$	$-4C^2$	0	0	S^2	$4C^2$

As an example, the expansion of $\langle e''_{114}\rangle$ equals $M_1A + M_2D + M_3D$, which in full reads:

$$\begin{aligned}\langle e''_{114}\rangle = (1/8)\Big[&e_{111}0 + e_{112}(-3CS) + e_{113}(3CS) + e_{114}\big(3(C^2-S^2)\big)\\ &+ \cdots + e_{166}(2CS)\Big] + (-C/8)\Big[e_{211}0 + \cdots + e_{216}(-S)\\ &+ \cdots + e_{246}\big(-2C(2C^2+S^2)\big)\cdots + e_{266}0\Big]\\ &+ (-S/8)\Big[e_{311}0 + \cdots + e_{316}(-S) + \cdots\\ &+ e_{346}\big(-2C(2C^2+S^2)\big) + \cdots + e_{366}0\Big].\end{aligned}$$

It will be seen that the majuscules (x_1 rotation) and minuscules (x_2 rotation) of the same alphabetic letter appearing in Tables 9, 10 and 13, 14 contain the same entries, albeit not in the same order, and with admixtures of sign reversals.

The 25 surviving triclinic $\langle e''\rangle$ coefficients are further reduced in number when particularized for classes of higher symmetry. Classes 1[63], 4[15], $\bar{4}$[14], 3[21], 6[11], and $\bar{6}$[10] retain all 25 $\langle e''\rangle$ coefficients. Classes m[34], $mm2$[17], 4mm [10], 3m[13], 6mm[8], and $\bar{6}m2$[5] are diminished to 17 $\langle e''\rangle$ survivors: $\langle e''_{115}\rangle$, $\langle e''_{125}\rangle$, $\langle e''_{135}\rangle$, $\langle e''_{146}\rangle$, $\langle e''_{214}\rangle$, $\langle e''_{224}\rangle$, $\langle e''_{234}\rangle$, $\langle e''_{256}\rangle$, $\langle e''_{311}\rangle$, $\langle e''_{312}\rangle$, $\langle e''_{313}\rangle$, $\langle e''_{322}\rangle$, $\langle e''_{323}\rangle$, $\langle e''_{333}\rangle$, $\langle e''_{344}\rangle$, $\langle e''_{355}\rangle$ and $\langle e''_{366}\rangle$. Classes 2[29], 222[12], 422[5], $\bar{4}2m$[7], 32[8], 622[3], 23[4] and 432[1] are further diminished to eight survivors: $\langle e''_{114}\rangle$, $\langle e''_{124}\rangle$, $\langle e''_{134}\rangle$, $\langle e''_{156}\rangle$, $\langle e''_{215}\rangle$, $\langle e''_{225}\rangle$, $\langle e''_{235}\rangle$ and $\langle e''_{246}\rangle$. Class $\bar{4}3m$[3] has no surviving coefficients. In square brackets above are the numbers of independent rank 5 coefficients for each point group (Grimmer, 2007). Given below are results for four classes of importance for micro- and nano-electronics.

5.3.2. Hexagonal, Laue VIb, class 6*mm*

Class 6mm possesses eight independent $e_{f\lambda\mu}$: $e_{115} = e_{224}$, $e_{125} = e_{214}$, $e_{135} = e_{234}$, $e_{311} = e_{322}$, $e_{312}, e_{313} = e_{323}$, e_{333} and $e_{344} = e_{355}$, with auxiliary relations $e_{146} = e_{256} = (1/2)(e_{115} - e_{125})$, and $e_{366} = e_{256} = (1/2)(e_{311} - e_{312})$. Each of the 17 $\langle e''\rangle$ results are the same for both x_1 and x_2 rotations and are given in Table 15.

5.3.3. Cubic, Laue VIIa, class 23

The four independent $e_{f\lambda\mu}$ of class 23 are: $e_{114} = e_{225} = e_{336}$, $e_{124} = e_{235} = e_{316}$, $e_{134} = e_{215} = e_{326}$, and $e_{156} = e_{246} = e_{345}$. The eight $\langle e''\rangle$ survivors of class 23 are identical with the vanishing members of class 6mm, but with the further relations: $\langle e''_{225}\rangle = -\langle e''_{114}\rangle$, $\langle e''_{215}\rangle = -\langle e''_{124}\rangle$, $\langle e''_{235}\rangle = -\langle e''_{134}\rangle$, and $\langle e''_{246}\rangle = -\langle e''_{156}\rangle$, for both rotations. The final results are: $\langle e''_{114}\rangle = \langle e''_{156}\rangle = -\langle e''_{246}\rangle = -\langle e''_{225}\rangle = (1/8)(1 - 5C^2S^2)(e_{124} - e_{134})$, $\langle e''_{124}\rangle = -\langle e''_{215}\rangle =$

Table 15
Explicit expressions for the 17 surviving $\langle e'' \rangle$ in terms of the unrotated $e_{\lambda\mu\nu}$ for Laue group VIb, class 6*mm*.

Results are identical for both x_1 and x_2 rotations. Table is in two parts, and is to be read as: $8\langle e''_{\lambda\mu\nu}\rangle = [\,]e_{115} + [\,]e_{125} + [\,]e_{135} + [\,]e_{311} + [\,]e_{312} + [\,]e_{313} + [\,]e_{333} + [\,]e_{344}$.

	e_{115}	e_{125}	e_{135}	e_{311}
$8\langle e''_{115}\rangle$	$4C^3(3C^2-1)$	0	$12C^3S^2$	$-CS^2(3C^2+1)$
$8\langle e''_{125}\rangle$	$-4C^3S^2$	$8C^3$	$4C^3S^2$	$4CS^4$
$8\langle e''_{135}\rangle$	$16C^3S^2$	0	$8C^3(C^2-S^2)$	$-4CS^4$
$8\langle e''_{146}\rangle$	$4C^5$	$-4C^3$	$4C^3S^2$	$-CS^2(1+C^2)$
$8\langle e''_{214}\rangle$	$-4C^3S^2$	$8C^3$	$4C^3S^2$	CS^4
$8\langle e''_{224}\rangle$	$4C^3(2C^2-S^2)$	0	$12C^3S^2$	$-C(1+3C^2)S^2$
$8\langle e''_{234}\rangle$	$16C^3S^2$	0	$8C^3(C^2-S^2)$	$-4CS^4$
$8\langle e''_{256}\rangle$	$4C^5$	$-4C^3$	$4C^3S^2$	$C(C^4-1)$
$8\langle e''_{311}\rangle$	$-4CS^2(3C^2+1)$	0	$-12CS^4$	$C(3C^4+2C^2+3)$
$8\langle e''_{312}\rangle$	$4CS^4$	$-16CS^2$	$-4CS^4$	CS^4
$8\langle e''_{313}\rangle$	$8C(C^2-S^2)S^2$	$8CS^2$	$-8C(C^2-S^2)S^2$	$4C^3S^2$
$8\langle e''_{322}\rangle$	$-4C(1+3C^2)S^2$	0	$-12CS^4$	$C(3C^4+2C^2+3)$
$8\langle e''_{323}\rangle$	$8C(C^2-S^2)S^2$	$8CS^2$	$-8C(C^2-S^2)S^2$	$4C^3S^2$
$8\langle e''_{333}\rangle$	$32CS^4$	0	$32C^3S^2$	$8CS^4$
$8\langle e''_{344}\rangle$	$4C[1+2(C^2-S^2)]S^2$	$-4CS^2$	$-8C(C^2-S^2)S^2$	$2CS^2(2C^2+1)$
$8\langle e''_{355}\rangle$	$4C[1+2(C^2-S^2)]S^2$	$-4CS^2$	$-8C(C^2-S^2)S^2$	$2CS^2(2C^2+1)$
$8\langle e''_{366}\rangle$	$-4C(C^2+1)S^2$	$8CS^2$	$-4CS^4$	$C(C^2+1)^2$

	e_{312}	e_{313}	e_{333}	e_{344}
$8\langle e''_{115}\rangle$	0	$CS^2[1+3(C^2-S^2)]$	$3CS^4$	$2CS^2[1+3(C^2-S^2)]$
$8\langle e''_{125}\rangle$	$-4CS^2$	$2CS^2(C^2+1)$	CS^4	$-4CS^4$
$8\langle e''_{135}\rangle$	0	$-4CS^2(C^2-S^2)$	$4C^3S^2$	$-8CS^2(C^2-S^2)$
$8\langle e''_{146}\rangle$	$2CS^2$	$-2CS^4$	CS^4	$4C^3S^2$
$8\langle e''_{214}\rangle$	$-4CS^2$	$2CS^2(C^2+1)$	CS^4	$-4CS^4$
$8\langle e''_{224}\rangle$	0	$2CS^2(3C^2-1)$	$3CS^4$	$4CS^2(3C^2-1)$
$8\langle e''_{234}\rangle$	0	$-4CS^2(C^2-S^2)$	$4C^3S^2$	$-8CS^2(C^2-S^2)$
$8\langle e''_{256}\rangle$	$2CS^2$	$-2CS^4$	CS^4	$4C^3S^2$
$8\langle e''_{311}\rangle$	0	$2CS^2(3C^2+1)$	$3CS^4$	$4CS^2(3C^2+1)$
$8\langle e''_{312}\rangle$	$8C^3$	$2CS^2(C^2+3)$	CS^4	$-4CS^4$
$8\langle e''_{313}\rangle$	$4CS^2$	$4C(C^2+C^4+S^4)$	$4C^3S^2$	$-16C^3S^2$
$8\langle e''_{322}\rangle$	0	$2C(3C^2+1)S^2$	$3CS^4$	$4C(1+3C^2)S^2$
$8\langle e''_{323}\rangle$	$4CS^2$	$4C(C^2+C^4+S^4)$	$4C^3S^2$	$-16C^3S^2$
$8\langle e''_{333}\rangle$	0	$16C^3S^2$	$8C^5$	$32C^3S^2$
$8\langle e''_{344}\rangle$	$-2CS^2$	$-8C^3S^2$	$4C^3S^2$	$4C[C^2+(C^2-S^2)^2]$
$8\langle e''_{355}\rangle$	$-2CS^2$	$-8C^3S^2$	$4C^3S^2$	$4C[C^2+(C^2-S^2)^2]$
$8\langle e''_{366}\rangle$	$-4C^3$	$-2CS^4$	CS^4	$4C(C^2+1)S^2$

$(3/8)\langle e''_{114}\rangle$ and $\langle e''_{134}\rangle = -\langle e''_{235}\rangle = -(1/2)\langle e''_{114}\rangle$. The x_1 relations are converted to those for x_2, by the substitution: $e_{124} \rightarrow e_{134}$.

5.3.4. Cubic, Laue VIIb, class 432

This class is included here because its linear piezoelectric effect is identically zero; the nonlinear $e_{f\lambda\mu}$ provide a driving mechanism for future applications of materials in this class. This class has but one independent $e_{f\lambda\mu}$: $e_{124} = -e_{134} = -e_{215} = e_{235} = e_{316} = -e_{326}$. After averaging, both x_1 and x_2 rotations give identical results for the eight remaining $\langle e'' \rangle$. Furthermore, these are multiples of $(1 - 5C^2S^2)$ as follows: $\langle e''_{114}\rangle = \langle e''_{156}\rangle = -\langle e''_{225}\rangle = -\langle e''_{246}\rangle = (1/4)(1 - 5C^2S^2)e_{124}$; and $\langle e''_{124}\rangle = -\langle e''_{215}\rangle = (3/4)(1 - 5C^2S^2)e_{124}$; and $\langle e''_{235}\rangle = -\langle e''_{134}\rangle = (1 - 5C^2S^2)e_{124}$. These results follow from those of class 23 by setting $e_{124} = -e_{134}$ therein.

5.3.5. Cubic, Laue VIIb, class $\bar{4}3m$

This class possesses three independent $e_{f\lambda\mu}$: $e_{114} = e_{225} = e_{336}$; $e_{124} = e_{134} = e_{215} = e_{235} = e_{316} = e_{326}$; $e_{156} = e_{246} = e_{345}$. After averaging all $\langle e'' \rangle$ are zero; the rank 5 nonlinear piezo effect vanishes in class $\bar{4}3m$.

5.4. Rank 6, nonlinear elastic stiffnesses, $c^{(6)}$

A lucid paper by Murnaghan (1937) began the study of nonlinear elasticity. He treated isotropic solids, for which, to lowest order, three nonlinear coefficients suffice. This was extended to cubic solids by Birch (1947). Subsequently, many other treatments have followed, *e.g.* Thurston & Brugger (1964) and Brugger (1964); see also the references in Truesdell & Toupin (1960), Truesdell & Noll (1965) and Norris (2024). Among the contributors to this field should be noted those of Mindlin (Herrmann, 1974; Mindlin, 1989) and those of what might be called the 'school of Mindlin', *e.g.* Tiersten (1969), Baumhauer & Tiersten (1973), Lee *et al.* (1975), di Lorenzi & Tiersten (1975), Ancona & Tiersten (1980), Sinha (2001), Patel & Sinha (2015), Sinha & Wendt (2015). The study of nonlinear elasticity might have begun primarily as an academic exercise, but the results have now become of importance in a variety of disparate fields, such as determinations of thermal expansion (Sheard, 1958), light diffraction by sound waves (Melngailis *et al.*, 1963), lattice theories of crystals (Srinivasan, 1966), quartz resonator thermal and stress sensitivity compensation (Ballato, 1977), acoustoelastic characterization of materials (non-destructive evaluation) (Cantrell & Salama, 1991; Cantrell, 1994), Poisson's ratio considerations (Ballato, 2010), calculations of textured polycrystals (Kube & Turner, 2016), and seismology (Stern *et al.*, 2017).

Rank 6 tensors have $3^6 = 729$ coefficients in general, but the third-order nonlinear elastic coefficients $c^{(6)}$ for a triclinic crystal are reduced to 56 because the coefficients are symmetric in all three Voigt indices; the number of multiplicities of each coefficient are listed in Table 5, column 1 of Hearmon (1953). Whereas each of the 21 non-centrosymmetric point groups has a unique rank 5 piezoelectric matrix, the nonlinear elastic matrices are determined solely by the Laue group. In this sense, treating the rank 6 nonlinear elastic situation is somewhat simpler than that of rank 5 effects.

Fumi (1951, 1952*a*, 1952*b*) was the first to enumerate, accurately, these independent elastic coefficients for triclinic crystals; we hereby address his lament (Fumi, 1987). Brugger's much more cited and comprehensive paper (Brugger, 1965) on the subject contains, in Table 3, the inter-relationships between certain of the $c_{\lambda\mu\nu}$, albeit in a footnote with a number of entries that are typographically ambiguous. Some of these may be recovered from Sirotin & Shaskolskaya (1982). All are listed in Table 16. Table 17 provides the number of independent elastic coefficients, of various orders, as function of the Laue classes. When the 56 independent rank 6 elastic coefficients are subjected to the averaging procedure, the result is a reduction to 24 $\langle c''_{\lambda\mu\nu}\rangle$ coefficients. The indices of these are given in Table 18. Table 19 provides the number of rank 6 elastic coefficients for all Laue groups, as well as those that are independent, and those that survive the averaging procedure.

Table 16
Relations among the rank 6 elastic coefficients for Laue groups Va, Vb, VIa and VIb and for isotropy.

Lowercase letters in parentheses correspond to those in Table 3 of Brugger (1965).

Laue Va, Vb, VIa and VIb		
(a): $c_{122} = (c_{111} + c_{112} - c_{222})$	(b): $c_{146} = (1/2)(-c_{115} - 3c_{125})$	(c): $c_{156} = (1/2)(c_{114} + 3c_{124})$
(d): $c_{166} = (1/4)(-2c_{111} - c_{112} + 3c_{222})$	(e): $c_{224} = (-c_{114} - 2c_{124})$	(f): $c_{225} = (-c_{115} - 2c_{125})$
(g): $c_{246} = (1/2)(-c_{115} + c_{125})$	(h): $c_{256} = (1/2)(c_{114} - c_{124})$	(i): $c_{266} = (1/4)(2c_{111} - c_{112} - c_{222})$
(j): $c_{366} = (1/2)(c_{113} - c_{123})$	(k): $c_{456} = (1/2)(-c_{114} + c_{155})$	
Isotropy		
(l): $c_{144} = (1/2)(c_{112} - c_{123})$	(m): $c_{155} = (1/4)(c_{111} - c_{112})$	(n): $c_{456} = (1/8)(c_{111} - 3c_{112} + 2c_{123})$

Table 17
Number of independent second-, third-, fourth- and fifth-order elastic coefficients for all Laue classes.

The second-order results are given, *e.g.* in IEEE Standard on Piezoelectricity (1987), Cady (1946), Nye (1985). Those of the third order are given by Fumi (1951), Brugger (1965). Krishnamurty (1963) provides the fourth order, and those of the fifth order are found in Krishnamurty & Gopalakrishnamurty (1968). For isotropy, the number of independent coefficients is equal to one-half the tensor rank.

Laue → / Rank ↓	I	II	III	IVa	IVb	Va	Vb	VIa	VIb	VIIa	VIIb	Isotropy
	Number of independent coefficients											
4	21	13	9	7	6	7	6	5	5	3	3	2
6	56	32	20	16	12	20	14	12	10	8	6	3
8	126	70	42	36	25	42	28	24	19	14	11	4
10	252	136	78	68	44	84	52	46	33	26	18	5

Table 18
Indices of the 24 finite, averaged, elastic stiffnesses $\langle c''_{\lambda\mu\nu}\rangle$ for triclinic Laue group I.

111	112	113	122	123	133	144	145
155	166	222	223	233	244	245	255
266	333	344	355	366	446	456	556

Tables 20–43 provide the x_1 rotation results for these $\langle c''\rangle$, factored as powers of C^n. In the even-order ranks, terms such as $(C^{2n} + S^{2n})$ occur. These may always be reduced to a finite polynomial in (C^2S^2). The polynomial appears in the form $1 - n(C^2S^2) + R(C^2S^2)$, where $R(C^2S^2)$ is a finite polynomial with all positive coefficients, and of order no greater than $n/2$. For example, because $(C^2 + S^2) = 1$, it follows that $(C^2 + S^2)^2 = 1 - 2(C^2S^2)$; $(C^2 + S^2)^3 = 1 - 3(C^2S^2)$, *etc*. However, with the exception of the results for cubic class $\overline{4}3m$ given subsequently, it appears simpler to display the results factored as powers of C^n. Note that the table entries are to be divided by 16; that is, the expressions are to be read as $16\langle c''_{\lambda\mu\nu}\rangle = [\,]C^6 + [\,]C^5 + \cdots +$ $[\,]C^0$. For nano- and micro-electronic application, the most useful results are those in hexagonal class $6mm$ (Laue VIb), and cubic class $\overline{4}3m$ (Laue VIIb).

Hexagonal, Laue VIb, class $6mm$ has ten independent coefficients: c_{111}, c_{112}, c_{113}, c_{123}, c_{133}, c_{144}, c_{155}, c_{222}, c_{333} and c_{344}. Table 44 contains the 20 extant $6mm$, x_1 rotation, $\langle c''\rangle$ coefficients in terms of these. The table is split into two parts

Table 20
Expansion of rank 6, x_1 rotation, Laue group I (triclinic) averaged elastic stiffness $\langle c''_{111}\rangle$.

The expansions in Tables 20 to 43 are to be read as: $16\langle c''_{\lambda\mu\nu}\rangle = C^6[\,] + C^5[\,] + C^4[\,] + C^3[\,] + C^2[\,] + C[\,] + [\,]$. C and S are $\cos(\theta)$ and $\sin(\theta)$, respectively, where θ is the facet angle.

C^6	$5c_{222}$
C^5	$30c_{224}S$
C^4	$3c_{122} + 12c_{266} + 15c_{223}S^2 + 60c_{244}S^2$
C^3	$12c_{124}S + 24c_{256}S + 24c_{466}S + 60c_{234}S^3 + 40c_{444}S^3$
C^2	$3c_{112} + 12c_{166} + 6c_{123}S^2 + 12c_{144}S^2 + 15c_{233}S^4 + 12c_{255}S^2 + 60c_{344}S^4 + 12c_{366}S^2 + 48c_{456}S^2$
C^1	$6c_{114}S + 24c_{156}S + 12c_{134}S^3 + 30c_{334}S^5 + 24c_{356}S^3 + 24c_{455}S^3$
C^0	$5c_{111} + 3c_{113}S^2 + 3c_{133}S^4 + 12c_{155}S^2 + 5c_{333}S^6 + 12c_{355}S^4$

Table 21
Expansion of rank 6, x_1 rotation, Laue group I (triclinic) averaged elastic stiffness $\langle c''_{112}\rangle$.

See expansion rule in caption to Table 20.

C^6	c_{222}
C^5	$6c_{224}S$
C^4	$7c_{122} - 4c_{266} + 3c_{223}S^2 + 12c_{244}S^2$
C^3	$28c_{124}S - 8c_{256}S - 8c_{466}S + 12c_{234}S^3 + 8c_{444}S^3$
C^2	$7c_{112} - 4c_{166} + 14c_{123}S^2 + 28c_{144}S^2 + 3c_{233}S^4 - 4c_{255}S^2 + 12c_{344}S^4 - 4c_{366}S^2 - 16c_{456}S^2$
C^1	$14c_{114}S - 8c_{156}S + 28c_{134}S^3 + 6c_{334}S^5 - 8c_{356}S^3 - 8c_{445}S^3$
C^0	$c_{111} + 7c_{113}S^2 + 7c_{133}S^4 - 4c_{155}S^2 + c_{333}S^6 - 4c_{355}S^4$

Table 19
Number of rank 6 elastic coefficients for all Laue groups.

The row labeled 'total' lists the number of $c_{\lambda\mu\nu}$ entries; the row below it lists the number of these that are independent. The last row gives the number of finite $\langle c''_{\lambda\mu\nu}\rangle$ entries. In Laue groups I, II, IVa, Va and VIa all of the 24 entries enumerated in Table 18 exist. In Laue groups III, IVb, Vb, VIb, VIIa and VIIb the relations $\langle c''_{145}\rangle = \langle c''_{245}\rangle = \langle c''_{446}\rangle = \langle c''_{556}\rangle \equiv 0$ reduce the number of finite entries to 20. In Laue groups VIb and VIIb the following equalities occur: $\langle c''_{111}\rangle = \langle c''_{222}\rangle$, $\langle c''_{112}\rangle = \langle c''_{122}\rangle$, $\langle c''_{113}\rangle = \langle c''_{223}\rangle$, $\langle c''_{133}\rangle = \langle c''_{233}\rangle$, $\langle c''_{155}\rangle = \langle c''_{244}\rangle$, $\langle c''_{166}\rangle = \langle c''_{266}\rangle$, and $\langle c''_{344}\rangle = \langle c''_{355}\rangle$, further reducing the number of relations to 13; see Tables 44 and 45. For isotropic substances, all 20 finite $\langle c''_{\lambda\mu\nu}\rangle$ are obviously equal to the corresponding unrotated $c_{\lambda\mu\nu}$ values.

System → / Laue →	Triclinic I	Monoclinic II	Rhombic III	Tetragonal IVa	Tetragonal IVb	Trigonal Va	Trigonal Vb	Hexagonal VIa	Hexagonal VIb	Cubic VIIa	Cubic VIIb	Isotropic (VIII)
Total	56	32	20	28	20	50	31	28	20	20	20	20
Independent	56	32	20	16	12	20	14	12	10	8	6	3
Finite $\langle c''_{\lambda\mu\nu}\rangle$	24	24	20	24	20	24	20	24	20	20	20	20

Table 22
Expansion of rank 6, x_1 rotation, Laue group I (triclinic) averaged elastic stiffness $\langle c''_{113}\rangle$.

See the expansion rule in caption to Table 20.

C^6	$6c_{223}$
C^5	$24c_{234}S - 12c_{224}S$
C^4	$4c_{123} + 8c_{366} + 6c_{222}S^2 + 12c_{233}S^2 - 48c_{244}S^2 + 24c_{344}S^2$
C^3	$8c_{134}S - 8c_{124}S + 16c_{356}S - 16c_{466}S + 24c_{224}S^3 - 24c_{234}S^3 + 24c_{334}S^3 - 48c_{444}S^3$
C^2	$6c_{113} + 4c_{122}S^2 + 4c_{133}S^2 + 12c_{223}S^4 - 16c_{144}S^2 + 6c_{333}S^4 + 24c_{244}S^4 - 48c_{344}S^4 + 8c_{355}S^2 + 8c_{266}S^2 - 32c_{456}S^2$
C^1	$8c_{124}S^3 - 12c_{114}S - 8c_{134}S^3 + 24c_{234}S^5 - 12c_{334}S^5 + 16c_{256}S^3 - 16c_{455}S^3$
C^0	$6c_{112}S^2 + 4c_{123}S^4 + 6c_{233}S^6 + 8c_{255}S^4$

Table 23
Expansion of rank 6, x_1 rotation, Laue group I (triclinic) averaged elastic stiffness $\langle c''_{122}\rangle$.

See the expansion rule in caption to Table 20.

C^6	c_{222}
C^5	$6c_{224}S$
C^4	$7c_{122} - 4c_{266} + 3c_{223}S^2 + 12c_{244}S^2$
C^3	$4(7c_{124} - 2c_{256} - 2c_{466})S + 4(3c_{234} + 2c_{444})S^3$
C^2	$7c_{112} - 4c_{166} + 14c_{123}S^2 + 28c_{144}S^2 + 3c_{233}S^4 - 4c_{255}S^2 + 12c_{344}S^4 - 4c_{366}S^2 - 16c_{456}S^2$
C^1	$2(7c_{114}S - 4c_{156}S + 14c_{134}S^3 + 3c_{334}S^5 - 4c_{356}S^3 - 4c_{455}S^3)$
C^0	$c_{111} + 7c_{113}S^2 + 7c_{133}S^4 - 4c_{155}S^2 + c_{333}S^6 - 4c_{355}S^4$

Table 24
Expansion of rank 6, x_1 rotation, Laue group I (triclinic) averaged elastic stiffness $\langle c''_{123}\rangle$.

See the expansion rule in caption to Table 20.

C^6	$2c_{223}$
C^5	$4(2c_{234} - c_{224})S$
C^4	$2(6c_{123} - 4c_{366} + c_{222}S^2 + 2c_{233}S^2 - 8c_{244}S^2 + 4c_{344}S^2)$
C^3	$8(3c_{134}S - 3c_{124}S - 2c_{356}S + 2c_{466}S + c_{224}S^3 - c_{234}S^3 + c_{334}S^3 - 2c_{444}S^3)$
C^2	$2(c_{113} + 6c_{122}S^2 + 6c_{133}S^2 + 2c_{223}S^4 - 24c_{144}S^2 + c_{333}S^4 + 4c_{244}S^4 - 8c_{344}S^4 - 4c_{355}S^2 - 4c_{266}S^2 + 16c_{456}S^2)$
C^1	$4(6c_{124}S^3 - c_{114}S - 6c_{134}S^3 + 2c_{234}S^5 - c_{334}S^5 - 4c_{256}S^3 + 4c_{455}S^3)$
C^0	$2(c_{112}S^2 + 6c_{123}S^4 + c_{233}S^6 - 4c_{255}S^4)$

Table 25
Expansion of rank 6, x_1 rotation, Laue group I (triclinic) averaged elastic stiffness $\langle c''_{133}\rangle$.

See the expansion rule in caption to Table 20.

C^6	$8c_{233}$
C^5	$16(c_{334} - 2c_{234})S$
C^4	$8(c_{133} + 2c_{223}S^2 + c_{333}S^2 + 4c_{244}S^2 - 8c_{344}S^2)$
C^3	$32(c_{234}S^3 - c_{224}S^3 - c_{134}S - c_{334}S^3 + 2c_{444}S^3)$
C^2	$8(2c_{123}S^2 + c_{222}S^4 + 4c_{144}S^2 + 2c_{233}S^4 - 8c_{244}S^4 + 4c_{344}S^4)$
C^1	$16(c_{224}S^5 - 2c_{124}S^3 - 2c_{234}S^5)$
C^0	$8(c_{223}S^6 + c_{122}S^4)$

for reasons of formatting, and is to be read as $M\langle c''_{\lambda\mu\nu}\rangle = [\,]c_{111} + [\,]c_{112} + \cdots + [\,]c_{333} + [\,]c_{344}$. In this expression the multiplier M = 16, except it is 32 for $\langle c''_{144}\rangle$, $\langle c''_{155}\rangle = \langle c''_{244}\rangle$, $\langle c''_{255}\rangle$ and $\langle c''_{456}\rangle$. For each $c_{\lambda\mu\nu}$, the table entries, given schematically as square brackets above, contain four numbers, (a_n), in the expansion $[a_n\cos^{2n}(\theta)]$, where n = 3, 2, 1, 0. Taking $\langle c''_{111}\rangle = \langle c''_{222}\rangle$ as an example, the expansion reads: $16\langle c''_{111}\rangle = 16\langle c''_{222}\rangle = [9C^4 - 6C^2 + 5]c_{111} + [0]c_{112} + [-15C^6 + 9C^4 + 3C^2 + 3]c_{113} + \ldots + [-5C^6 + 15C^4 - 15C^2 + 5]c_{333} + [60C^6 - 108C^4 + 36C^2 + 12]c_{344}$, where $C = \cos(\theta)$, and θ is the facet angle.

Table 26
Expansion of rank 6, x_1 rotation, Laue group I (triclinic) averaged elastic stiffness $\langle c''_{144}\rangle$.

See the expansion rule in caption to Table 20.

C^6	$2c_{244}$
C^5	$4(c_{234} - c_{224} + c_{444})S$
C^4	$2(3c_{144} + 3c_{255} - 4c_{456} + c_{222}S^2 - 2c_{233}S^2 + c_{233}S^2 - 6c_{244}S^2 + 5c_{344}S^2)$
C^3	$4(3c_{134}S - 3c_{124}S - c_{256}S - 2c_{356}S + c_{455}S + 2c_{466}S + 2c_{224}S^3 - 4c_{234}S^3 + 2c_{334}S^3 - 2c_{444}S^3)$
C^2	$2(c_{155} + 3c_{122}S^2 - 6c_{123}S^2 + 3c_{133}S^2 + c_{223}S^4 - 6c_{144}S^2 - 2c_{233}S^4 + c_{333}S^4 + 5c_{244}S^4 + 4c_{255}S^2 - 6c_{344}S^4 - c_{355}S^2 - c_{266}S^2 + 4c_{366}S^2 - 4c_{456}S^2)$
C^1	$4(3c_{124}S^3 - c_{156}S - 3c_{134}S^3 + c_{234}S^5 - c_{334}S^5 - 2c_{256}S^3 + c_{444}S^5 - c_{356}S^3 + 2c_{455}S^3 + c_{466}S^3)$
C^0	$2(3c_{144}S^4 + c_{166}S^2 + c_{344}S^6 + 3c_{366}S^4 - 4c_{456}S^4)$

Table 27
Expansion of rank 6, x_1 rotation, Laue group I (triclinic) averaged elastic stiffness $\langle c''_{145}\rangle$.

See the expansion rule in caption to Table 20.

C^6	0
C^5	$4(c_{446} - c_{245})$
C^4	$4(c_{225} - c_{235} - c_{246} + 2c_{346} - c_{445})S$
C^3	$4(c_{145} - c_{556} - c_{236}S^2 + c_{245}S^2 + c_{336}S^2 - c_{345}S^2)$
C^2	$4(c_{135}S - c_{125}S - c_{146}S - c_{555}S + 2c_{566}S + c_{225}S^3 - c_{235}S^3 - c_{246}S^3 + c_{346}S^3)$
C^1	$4(c_{126}S^2 - c_{136}S^2 - c_{145}S^2 - c_{236}S^4 + 2c_{245}S^4 + c_{336}S^4 - c_{345}S^4 - c_{446}S^4 + 2c_{556}S^2 - c_{666}S^2)$
C^0	$4(c_{146}S^3 - c_{346}S^5 + c_{445}S^5 - c_{566}S^3)$

Table 28
Expansion of rank 6, x_1 rotation, Laue group I (triclinic) averaged elastic stiffness $\langle c''_{155}\rangle$.

See the expansion rule in caption to Table 20.

C^6	$6c_{244}$
C^5	$12(c_{234} - c_{224} + c_{444})S$
C^4	$2(c_{144} + c_{255} + 4c_{456} + 3c_{222}S^2 - 6c_{223}S^2 + 3c_{233}S^2 - 18c_{244}S^2 + 15c_{344}S^2)$
C^3	$4(c_{134}S - c_{124}S - 3c_{256}S + 2c_{356}S + 3c_{455}S - 2c_{466}S + 6c_{224}S^3 - 12c_{234}S^3 + 6c_{334}S^3 - 6c_{444}S^3)$
C^2	$2(3c_{155} + c_{122}S^2 - 2c_{123}S^2 + c_{133}S^2 + 3c_{223}S^4 - 2c_{144}S^2 - 6c_{233}S^4 + 3c_{333}S^4 + 15c_{244}S^4 - 4c_{255}S^2 - 18c_{344}S^4 + 5c_{355}S^2 + 5c_{266}S^2 - 4c_{366}S^2 - 12c_{456}S^2)$
C^1	$4(c_{124}S^3 - 3c_{156}S - c_{134}S^3 + 3c_{234}S^5 - 3c_{334}S^5 + 2c_{256}S^3 + 3c_{444}S^5 - 3c_{356}S^3 - 2c_{455}S^3 + 3c_{466}S^3)$
C^0	$2(c_{144}S^4 + 3c_{166}S^2 + 3c_{344}S^6 + c_{366}S^4 + 4c_{456}S^4)$

Table 29
Expansion of rank 6, x_1 rotation, Laue group I (triclinic) averaged elastic stiffness $\langle c''_{166}\rangle$.

See the expansion rule in caption to Table 20.

C^6	c_{222}
C^5	$6c_{224}S$
C^4	$4c_{266} - c_{122} + 3c_{223}S^2 + 12c_{244}S^2$
C^3	$8c_{256}S - 4c_{124}S + 8c_{466}S + 12c_{234}S^3 + 8c_{444}S^4$
C^2	$4c_{166} - c_{112} - 2c_{123}S^2 - 4c_{144}S^2 + 3c_{233}S^4 + 4c_{255}S^2 + 12c_{344}S^4 + 4c_{366}S^2 + 16c_{456}S^2$
C^1	$8c_{156}S - 2c_{114}S - 4c_{134}S^3 + 6c_{334}S^5 + 8c_{356}S^3 + 8c_{455}S^3$
C^0	$c_{111} - c_{113}S^2 - c_{133}S^4 + 4c_{155}S^2 + c_{333}S^6 + 4c_{355}S^4$

Cubic (Laue VIIb) class $\overline{4}3m$ has six independent coefficients: c_{111}, c_{112}, c_{123}, c_{144}, c_{155} and c_{456}. In Table 45 are given the 20 surviving $\overline{4}3m$, x_1 rotation, $\langle c'\rangle$ coefficients, formatted with two values for each $c_{\lambda\mu\nu}$, an integer plus the coefficient of $(CS)^2$.

Table 30
Expansion of rank 6, x_1 rotation, Laue group I (triclinic) averaged elastic stiffness $\langle c''_{222}\rangle$.

See the expansion rule in caption to Table 20.

C^6	$5c_{222}$
C^5	$30c_{224}S$
C^4	$3(c_{122} + 4c_{266} + 5c_{223}S^2 + 20c_{244}S^2)$
C^3	$4(3c_{124}S + 6c_{256}S + 6c_{466}S + 15c_{234}S^3 + 10c_{444}S^3)$
C^2	$3(c_{112} + 4c_{166} + 2c_{123}S^2 + 4c_{144}S^2 + 5c_{233}S^4 + 4c_{255}S^2 + 20c_{344}S^4 + 4c_{366}S^2 + 16c_{456}S^2)$
C^1	$6(c_{114}S + 4c_{156}S + 2c_{134}S^3 + 5c_{334}S^5 + 4c_{356}S^3 + 4c_{455}S^3)$
C^0	$5c_{111} + 3c_{113}S^2 + 3c_{133}S^4 + 12c_{155}S^2 + 5c_{333}S^6 + 12c_{355}S^4$

Table 31
Expansion of rank 6, x_1 rotation, Laue group I (triclinic) averaged elastic stiffness $\langle c''_{223}\rangle$.

See the expansion rule in caption to Table 20.

C^6	$6c_{223}$
C^5	$12(2c_{234} - c_{224})S$
C^4	$2(2c_{123} + 4c_{366} + 3c_{222}S^2 + 6c_{233}S^2 - 24c_{244}S^2 + 12c_{344}S^2)$
C^3	$8(c_{134}S - c_{124}S + 2c_{356}S - 2c_{466}S + 3c_{224}S^3 - 3c_{234}S^3 + 3c_{334}S^3 - 6c_{444}S^3)$
C^2	$2(3c_{113} + 2c_{122}S^2 + 2c_{133}S^2 + 6c_{223}S^4 - 8c_{144}S^2 + 3c_{333}S^4 + 12c_{244}S^4 - 24c_{344}S^4 + 4c_{355}S^2 + 4c_{266}S^2 - 16c_{456}S^2)$
C^1	$4(2c_{124}S^3 - 3c_{114}S - 2c_{134}S^3 + 6c_{234}S^5 - 3c_{334}S^5 + 4c_{256}S^3 - 4c_{455}S^3)$
C^0	$2(3c_{112}S^2 + 2c_{123}S^4 + 3c_{233}S^6 + 4c_{255}S^4)$

Table 32
Expansion of rank 6, x_1 rotation, Laue group I (triclinic) averaged elastic stiffness $\langle c''_{233}\rangle$.

See the expansion rule in caption to Table 20.

C^6	$8c_{233}$
C^5	$16(c_{334} - 2c_{234})S$
C^4	$8(c_{133} + 2c_{223}S^2 + c_{333}S^2 + 4c_{244}S^2 - 8c_{344}S^2)$
C^3	$32(c_{234}S^3 - c_{224}S^3 - c_{134}S - c_{334}S^3 + 2c_{444}S^3)$
C^2	$8(2c_{123}S^2 + c_{222}S^4 + 4c_{144}S^2 + 2c_{233}S^4 - 8c_{244}S^4 + 4c_{344}S^4)$
C^1	$16(c_{224}S^5 - 2c_{124}S^3 - 2c_{234}S^5)$
C^0	$8(c_{223}S^6 + c_{122}S^4)$

Table 33
Expansion of rank 6, x_1 rotation, Laue group I (triclinic) averaged elastic stiffness $\langle c''_{244}\rangle$.

See the expansion rule in caption to Table 20.

C^6	$6c_{244}$
C^5	$12(c_{234} - c_{224} + c_{444})S$
C^4	$2(c_{144} + c_{255} + 4c_{456} + 3c_{222}S^2 - 6c_{223}S^2 + 3c_{233}S^2 - 18c_{244}S^2 + 15c_{344}S^2)$
C^3	$4(c_{134}S - c_{124}S - 3c_{256}S + 2c_{356}S + 3c_{455}S - 2c_{466}S + 6c_{224}S^3 - 12c_{234}S^3 + 6c_{334}S^3 - 6c_{444}S^3)$
C^2	$2(3c_{155} + c_{122}S^2 - 2c_{123}S^2 + c_{133}S^2 + 3c_{223}S^4 - 2c_{144}S^2 - 6c_{233}S^4 + 3c_{333}S^4 + 15c_{244}S^4 - 4c_{255}S^2 - 18c_{344}S^4 + 5c_{355}S^2 + 5c_{266}S^2 - 4c_{366}S^2 + 12c_{456}S^2)$
C^1	$4(c_{124}S^3 - 3c_{156}S - c_{134}S^3 + 3c_{234}S^5 - 3c_{334}S^5 + 2c_{256}S^3 + 3c_{444}S^5 - 3c_{356}S^3 - 2c_{455}S^3 + 3c_{466}S^3)$
C^0	$2(c_{144}S^4 + 3c_{166}S^2 + 3c_{344}S^6 + c_{366}S^4 + 4c_{456}S^4)$

All the rank 6, x_2 rotation formulas may be obtained from those for x_1 rotation simply by making the following substitutions of the $c_{\lambda\mu\nu}$ in Tables 20–45: $1 \rightarrow 2$, $2 \rightarrow 1$, $3 \rightarrow 3$, $4 \rightarrow -5$, $5 \rightarrow 4$ and $6 \rightarrow -6$.

5.5. Ferroelectricity: a different type of nonlinearity

Of the 32 crystallographic point groups, 21 are noncentrosymmetric (acentric). Fig. 1 in Halasyamani & Poeppelmeier (1998) provides an insightful Venn diagram showing various property interrelationships between these noncentrosymmetric (acentric) point groups. With the exception of class 432, all noncentrosymmetric (acentric) groups allow linear piezoelectricity. The 20 piezoelectric classes are further divided according to whether they do, or do not, possess a spontaneous electric dipole moment, *i.e.* are polar or non-

Table 34
Expansion of rank 6, x_1 rotation, Laue group I (triclinic) averaged elastic stiffness $\langle c''_{245}\rangle$.

See the expansion rule in caption to Table 20.

C^6	0
C^5	$4(c_{245} - c_{446})$
C^4	$4(c_{235} - c_{225} + c_{246} - 2c_{346} + c_{445})S$
C^3	$4(c_{556} - c_{145} + c_{236}S^2 - c_{245}S^2 - c_{336}S^2 + c_{345}S^2)$
C^2	$4(c_{125}S - c_{135}S + c_{146}S + c_{555}S - 2c_{566}S - c_{225}S^3 + c_{235}S^3 + c_{246}S^3 - c_{346}S^3)$
C^1	$4(c_{136}S^2 - c_{126}S^2 + c_{145}S^2 + c_{236}S^4 - 2c_{245}S^4 - c_{336}S^4 + c_{345}S^4 + c_{446}S^4 - 2c_{556}S^2 + c_{666}S^2)$
C^0	$4(c_{346}S^5 - c_{146}S^3 - c_{445}S^5 + c_{566}S^3)$

Table 35
Expansion of rank 6, x_1 rotation, Laue group I (triclinic) averaged elastic stiffness $\langle c''_{255}\rangle$.

See the expansion rule in caption to Table 20.

C^6	$2c_{244}$
C^5	$4(c_{234} - c_{224} + c_{444})S$
C^4	$2(3c_{144} + 3c_{255} - 4c_{456} + c_{222}S^2 - 2c_{223}S^2 + c_{233}S^2 - 6c_{244}S^2 + 5c_{344}S^2)$
C^3	$4(3c_{134}S - 3c_{124}S - c_{256}S - 2c_{356}S + c_{455}S + 2c_{466}S + 2c_{224}S^3 - 4c_{234}S^3 + 2c_{334}S^3 - 2c_{444}S^3)$
C^2	$2(c_{155} + 3c_{122}S^2 - 6c_{123}S^2 + 3c_{133}S^2 + c_{223}S^4 - 6c_{144}S^2 - 2c_{233}S^4 + c_{333}S^4 + 5c_{244}S^4 + 4c_{255}S^2 - 6c_{344}S^4 - c_{355}S^2 - c_{266}S^2 + 4c_{366}S^2 - 4c_{456}S^2)$
C^1	$4(3c_{124}S^3 - c_{156}S - 3c_{134}S^3 + c_{234}S^5 - c_{334}S^5 - 2c_{256}S^3 + c_{444}S^5 - c_{356}S^3 + 2c_{455}S^3 + c_{466}S^3)$
C^0	$2(3c_{144}S^4 + c_{166}S^2 + c_{344}S^6 + 3c_{366}S^4 + 4c_{456}S^4)$

Table 36
Expansion of rank 6, x_1 rotation, Laue group I (triclinic) averaged elastic stiffness $\langle c''_{266}\rangle$.

See the expansion rule in caption to Table 20.

C^6	c_{222}
C^5	$6c_{224}S$
C^4	$4c_{266} - c_{122} + 3c_{223}S^2 + 12c_{244}S^2$
C^3	$4(2c_{256}S - c_{124}S + 2c_{466}S + 3c_{234}S^3 + 2c_{444}S^3)$
C^2	$4c_{166} - c_{112} - 2c_{123}S^2 - 4c_{144}S^2 + 3c_{233}S^4 + 4c_{255}S^2 + 12c_{344}S^4 + 4c_{366}S^2 + 16c_{456}S^2$
C^1	$2(4c_{156}S - c_{114}S - 2c_{134}S^3 + 3c_{334}S^5 + 4c_{356}S^3 + 4c_{455}S^3)$
C^0	$c_{111} - c_{113}S^2 - c_{133}S^4 + 4c_{155}S^2 + c_{333}S^6 + 4c_{355}S^4$

Table 37
Expansion of rank 6, x_1 rotation, Laue group I (triclinic) averaged elastic stiffness $\langle c''_{333}\rangle$.

See the expansion rule in caption to Table 20.

C^6	$16c_{333}$
C^5	$-96c_{334}S$
C^4	$48(c_{233} + 4c_{344})S^2$
C^3	$-64(3c_{234} + 2c_{444})S^3$
C^2	$48(c_{223} + 4c_{244})S^4$
C^1	$-96c_{224}S^5$
C^0	$16c_{222}S^6$

Table 38
Expansion of rank 6, x_1 rotation, Laue group I (triclinic) averaged elastic stiffness $\langle c''_{344}\rangle$.

See the expansion rule in caption to Table 20.

C^6	$8c_{344}$
C^5	$16(c_{334} - c_{234} - c_{444})S$
C^4	$8(c_{355} + c_{223}S^2 - 2c_{233}S^2 + c_{333}S^2 + 5c_{244}S^2 - 6c_{344}S^2)$
C^3	$16(4c_{234}S^3 - c_{455}S - 2c_{224}S^3 - c_{356}S - 2c_{334}S^3 + 2c_{444}S^3)$
C^2	$8(c_{222}S^4 - 2c_{223}S^4 + c_{233}S^4 - 6c_{244}S^4 + c_{255}S^2 + 5c_{344}S^4 + c_{366}S^2 + 4c_{456}S^2)$
C^1	$16(c_{224}S^5 - c_{234}S^5 - c_{256}S^3 - c_{444}S^5 - c_{466}S^3)$
C^0	$8(c_{244}S^6 + c_{266}S^4)$

Table 39
Expansion of rank 6, x_1 rotation, Laue group I (triclinic) averaged elastic stiffness $\langle c''_{355}\rangle$.

See the expansion rule in caption to Table 20.

C^6	$8c_{344}$
C^5	$16(c_{334} - c_{234} - c_{444})S$
C^4	$8(c_{355} + c_{223}S^2 - 2c_{233}S^2 + c_{333}S^2 + 5c_{244}S^2 - 6c_{344}S^2)$
C^3	$16(4c_{234}S^3 - c_{455}S - 2c_{224}S^3 - c_{356}S - 2c_{334}S^3 + 2c_{444}S^3)$
C^2	$8(c_{222}S^4 - 2c_{223}S^4 + c_{233}S^4 - 6c_{244}S^4 + c_{255}S^2 + 5c_{344}S^4 + c_{366}S^2 + 4c_{456}S^2)$
C^1	$16(c_{224}S^5 - c_{234}S^5 - c_{256}S^3 - c_{444}S^5 - c_{466}S^3)$
C^0	$8(c_{244}S^6 + c_{266}S^4)$

Table 40
Expansion of rank 6, x_1 rotation, Laue group I (triclinic) averaged elastic stiffness $\langle c''_{366}\rangle$.

See the expansion rule in caption to Table 20.

C^6	$2c_{223}$
C^5	$4(2c_{234} - c_{224})S$
C^4	$2(4c_{366} - 2c_{123} + c_{222}S^2 + 2c_{233}S^2 - 8c_{244}S^2 + 4c_{344}S^2)$
C^3	$8(c_{124}S - c_{134}S + 2c_{356}S - 2c_{466}S + c_{224}S^3 - c_{234}S^3 + c_{334}S^3 - c_{444}S^3)$
C^2	$2(c_{113} - 2c_{122}S^2 - 2c_{133}S^2 + 2c_{223}S^4 + 8c_{144}S^2 + c_{333}S^4 + 4c_{244}S^4 - 8c_{344}S^4 + 4c_{355}S^2 + 4c_{266}S^2 - 16c_{456}S^2)$
C^1	$4(2c_{134}S^3 - 2c_{124}S^3 - c_{114}S + 2c_{234}S^5 - c_{334}S^5 + 4c_{256}S^3 - 4c_{455}S^3)$
C^0	$2(c_{112}S^2 - 2c_{123}S^4 + c_{233}S^6 + 4c_{255}S^4)$

Table 41
Expansion of rank 6, x_1 rotation, Laue group I (triclinic) averaged elastic stiffness $\langle c''_{446}\rangle$.

See the expansion rule in caption to Table 20.

C^6	0
C^5	$4(c_{446} - c_{245})$
C^4	$4(c_{225} - c_{235} - c_{246} + 2c_{346} - c_{445})S$
C^3	$4(c_{145} - c_{556} - c_{236}S^2 + c_{245}S^2 + c_{336}S^2 - c_{345}S^2)$
C^2	$4(c_{135}S - c_{125}S - c_{146}S - c_{555}S + 2c_{566}S + c_{225}S^3 - c_{235}S^3 - c_{246}S^3 + c_{346}S^3)$
C^1	$4(c_{126}S^2 - c_{136}S^2 - c_{145}S^2 - c_{236}S^4 + 2c_{245}S^4 + c_{336}S^4 - c_{345}S^4 - c_{446}S^4 + 2c_{556}S^2 - c_{666}S^2)$
C^0	$4(c_{146}S^3 - c_{346}S^5 + c_{445}S^5 - c_{566}S^3)$

Table 42
Expansion of rank 6, x_1 rotation, Laue group I (triclinic) averaged elastic stiffness $\langle c''_{456}\rangle$.

See the expansion rule in caption to Table 20.

C^6	$2c_{244}$
C^5	$4(c_{234} - c_{224} + c_{444})S$
C^4	$2(4c_{456} - c_{255} - c_{144} + c_{222}S^2 - 2c_{223}S^2 + c_{233}S^2 - 6c_{244}S^2 + 5c_{344}S^2)$
C^3	$4(c_{124}S - c_{134}S - c_{256}S + 2c_{356}S + c_{455}S - 2c_{466}S + 2c_{224}S^3 - 4c_{234}S^3 + 2c_{334}S^3 - 2c_{444}S^3)$
C^2	$2(c_{155} - c_{122}S^2 + 2c_{123}S^2 - c_{133}S^2 + c_{223}S^4 + 2c_{144}S^2 - 2c_{233}S^4 + c_{333}S^4 + 5c_{244}S^4 - 4c_{255}S^2 - 6c_{344}S^4 + 3c_{355}S^2 + 3c_{266}S^2 - 4c_{366}S^2 - 4c_{456}S^2)$
C^1	$4(c_{134}S^3 - c_{124}S^3 - c_{156}S + c_{234}S^5 - c_{334}S^5 + 2c_{256}S^3 + c_{444}S^5 - c_{356}S^3 - 2c_{455}S^3 + c_{466}S^3)$
C^0	$2(c_{166}S^2 - c_{144}S^4 + c_{344}S^6 - c_{366}S^4 + 4c_{456}S^4)$

Table 43
Expansion of rank 6, x_1 rotation, Laue group I (triclinic) averaged elastic stiffness $\langle c''_{556}\rangle$.

See the expansion rule in caption to Table 20.

C^6	0
C^5	$4(c_{245} - c_{446})$
C^4	$4(c_{235} - c_{225} + c_{246} - 2c_{346} + c_{445})S$
C^3	$4(c_{556} - c_{145} + c_{236}S^2 - c_{245}S^2 - c_{336}S^2 + c_{345}S^2)$
C^2	$4(c_{125}S - c_{135}S + c_{146}S + c_{555}S - 2c_{566}S - c_{225}S^3 + c_{235}S^3 + c_{246}S^3 - c_{346}S^3)$
C^1	$4(c_{136}S^2 - c_{126}S^2 + c_{145}S^2 + c_{236}S^4 - 2c_{245}S^4 - c_{336}S^4 + c_{345}S^4 + c_{446}S^4 - 2c_{556}S^2 + c_{666}S^2)$
C^0	$4(c_{346}S^5 - c_{146}S^3 - c_{445}S^5 + c_{566}S^3)$

polar. Materials in the ten polar classes exhibit pyroelectricity, a rank 1 (vectorial) effect relating charge production and temperature change (Chynoweth, 1956; Mason, 1971; Lang, 2005). The pyroelectrics are further subdivided into those whose electric polarization is, or is not, reversible upon imposition of a sufficiently strong electric field. Those allowing reversible polarization are called ferroelectrics. The relationship between polarization and the applied electric field describes a hysteresis loop, so the polarization depends on the material's previous history, and thus this nonlinearity is not readily amenable to a power series formulation like the other recoverable effects treated herein. Another example of nonlinear hysteretic behavior occurs with coupled elastic modes in finite piezoelectric resonators, where so-called 'activity dips' occur (Li *et al.*, 2026).

Discovery of the ferroelectric hysteretic effect is attributed to Valasek (1920, 1921, 1922, 1971) by Jaffe (1964, 1975). Jaffe also discusses unrecovered, classified reports, dated 1918, to the National Research Council by J. A. Anderson (Stanford University) and W. G. Cady (Wesleyan University) that he had seen; the contents of these reports, if subsequently recovered, would furnish material for a lively debate regarding priority. From his personal interactions with Jaffe, one author (AB), has no doubt as to the existence and contents of the reports.

5.6. Linear pyroelectric coefficients

Soon after the discovery of this effect, it was found experimentally that those few ferroelectric materials then known had much larger linear pyroelectric coefficients than ordinary polar crystals. This spurred a search for additional ferroelectrics, and determinations of their phenomenological elastic, piezoelectric, dielectric, and pyroelectric material coefficients (Shirane *et al.*, 1955; Pepinsky *et al.*, 1956; Pepinsky & Jona, 1957). The suitability of materials such as triglycine sulfate (TGS, monoclinic space group $P2_1$) for thermal devices utilizing the pyroelectric effect was recognized in the early 1960s (Hoshino *et al.*, 1957; Konstantinova *et al.*, 1960; Ballato, 1961). Since then the gamut of useful pyroelectric materials has dramatically increased (Srinivasan,

Table 44
Hexagonal, VIb, class $6mm$ $\langle c''\rangle$ coefficients, x_1 rotation.

Entries are to be divided by 16, except $\langle c''_{144}\rangle$, $\langle c''_{155}\rangle = \langle c''_{244}\rangle$, $\langle c''_{255}\rangle$ and $\langle c''_{456}\rangle$; these are to be divided by 32. For typographical clarity, the table is divided into two parts; see text for details.

	c_{111}	c_{112}	c_{113}	c_{123}	c_{133}
$\langle c''_{111}\rangle = \langle c''_{222}\rangle$	0 / 9 / −6 / 5	0	−15 / 9 / 3 / 3	0	15 / −27 / 9 / 3
$\langle c''_{112}\rangle = \langle c''_{122}\rangle$	0 / 5 / 2 / 1	0 / 8 / 8 / 0	−3 / 5 / −9 / 7	0 / −16 / 16 / 0	3 / 1 / −11 / 7
$\langle c''_{113}\rangle = \langle c''_{223}\rangle$	0 / −8 / 8 / 0	0 / −2 / −4 / 6	18 / −20 / 18 / 0	0 / 4 / −8 / 4	−18 / 26 / −14 / 6
$\langle c''_{123}\rangle$	0 / −8 / 8 / 0	0 / −14 / 12 / 2	6 / −12 / 6 / 0	0 / 28 / −24 / 12	−6 / −2 / 6 / 2
$\langle c''_{133}\rangle = \langle c''_{233}\rangle$	0 / 8 / −16 / 8	0 / 8 / −16 / 8	−24 / 40 / −24 / 8	0 / −16 / 16 / 0	24 / −24 / 16 / 0
$\langle c''_{144}\rangle$	0 / −10 / 12 / −2	0 / −13 / 14 / −1	12 / −18 / 0 / 6	0 / 26 / −20 / −6	−12 / −8 / 4 / 0
$\langle c''_{155}\rangle = \langle c''_{244}\rangle$	0 / −14 / 20 / −6	0 / 1 / 2 / −3	36 / −38 / 0 / 2	0 / −2 / 4 / −2	−36 / 56 / −20 / 0
$\langle c''_{166}\rangle = \langle c''_{266}\rangle$	0 / 1 / −2 / 1	0 / −2 / −2 / 0	−3 / 1 / 3 / −1	0 / 4 / −4 / 0	3 / −7 / 5 / −1
$\langle c''_{255}\rangle$	0 / −10 / 12 / −2	0 / −13 / 14 / −1	12 / −18 / 0 / 6	0 / 26 / −20 / −6	−12 / 8 / 4 / 0
$\langle c''_{333}\rangle$	0	0	48 / −96 / 48 / 0	0	−48 / 48 / 0 / 0
$\langle c''_{344}\rangle = \langle c''_{355}\rangle$	0 / 4 / −8 / 4	0 / −2 / 4 / −2	−24 / 36 / −12 / 0	0 / 4 / −4 / 0	24 / −32 / 8 / 0
$\langle c''_{366}\rangle$	0	0 / 6 / −8 / 2	6 / −4 / 6 / 0	0 / −12 / 8 / −4	−6 / 14 / −10 / 2
$\langle c''_{456}\rangle$	0 / −2 / 4 / −2	0 / 7 / −6 / −1	12 / −10 / 0 / −2	0 / −14 / 12 / 2	−12 / 24 / −12 / 0

	c_{144}	c_{155}	c_{222}	c_{333}	c_{344}
$\langle c''_{111}\rangle = \langle c''_{222}\rangle$	0	−60 / 36 / 12 / 12	5 / −6 / 9 / 0	−5 / 15 / −15 / 5	60 / −108 / 36 / 12
$\langle c''_{112}\rangle = \langle c''_{122}\rangle$	0 / −32 / 32 / 0	−12 / 20 / −4 / −4	1 / −6 / −3 / 0	−1 / 3 / −3 / 1	12 / −28 / 20 / −4
$\langle c''_{113}\rangle = \langle c''_{223}\rangle$	0 / 8 / −16 / 8	72 / −80 / 8 / 0	−6 / 12 / −6 / 0	6 / −12 / 6 / 0	−72 / 112 / −40 / 0
$\langle c''_{123}\rangle$	0 / 56 / −48 / −8	24 / −48 / 24 / 0	−2 / 12 / −10 / 0	2 / −4 / 2 / 0	−24 / 48 / −24 / 0
$\langle c''_{133}\rangle = \langle c''_{233}\rangle$	0 / −32 / 32 / 0	−96 / 160 / −64 / 0	8 / −24 / 24 / −8	−8 / 8 / 0 / 0	96 / −128 / 32 / 0
$\langle c''_{144}\rangle$	0 / 52 / −40 / 20	48 / −72 / 32 / −8	−4 / 15 / −14 / 3	4 / −8 / 4 / 0	−48 / 84 / −40 / 4
$\langle c''_{155}\rangle = \langle c''_{244}\rangle$	0 / −4 / 8 / −4	144 / −152 / 32 / 8	−12 / 21 / −18 / 9	12 / −24 / 12 / 0	−144 / 220 / −88 / 12
$\langle c''_{166}\rangle = \langle c''_{266}\rangle$	0 / 8 / −8 / 0	−12 / 4 / 4 / 4	1 / 0 / 3 / 0	−1 / 3 / −3 / 1	12 / −20 / 4 / 4
$\langle c''_{255}\rangle$	0 / 52 / −40 / 20	48 / −72 / 32 / −8	−4 / 15 / −14 / 3	4 / −8 / 4 / 0	−48 / 84 / −40 / 4
$\langle c''_{333}\rangle$	0	192 / −384 / 192 / 0	−16 / 48 / −48 / 16	16 / 0 / 0 / 0	−192 / 192 / 0 / 0
$\langle c''_{344}\rangle = \langle c''_{355}\rangle$	0 / 8 / −8 / 0	−96 / 144 / −56 / 8	8 / −18 / 12 / −2	−8 / 8 / 0 / 0	96 / −120 / 40 / 0
$\langle c''_{366}\rangle$	0 / −24 / 16 / 8	24 / −16 / −8 / 0	−2 / 0 / 2 / 0	2 / −4 / 2 / 0	−24 / 32 / −8 / 0
$\langle c''_{456}\rangle$	0 / −28 / 24 / −12	48 / −40 / 0 / 8	−4 / 3 / −2 / 3	4 / −8 / 4 / 0	−48 / 68 / −24 / 4

Table 45
Cubic, VIIb, class $\bar{4}3m$ $\langle c''\rangle$ coefficients, x_1 rotation.

All $\langle c''\rangle$ entries are to be divided by 16. The entries are to be read as, *e.g.* $16\langle c''_{111}\rangle = 16\langle c''_{222}\rangle = (10 - 15C^2S^2)c_{111} + (6 + 9C^2S^2)c_{112} + \ldots + (24 + 36C^2S^2)c_{155} + (48C^2S^2)c_{456}$, where C is $\cos(\theta)$, and S is $\sin(\theta)$, and θ is the facet angle.

$16\langle c''_{\lambda\mu\nu}\rangle$	c_{111}	c_{112}	c_{123}	c_{144}	c_{155}	c_{456}
$\langle c''_{111}\rangle = \langle c''_{222}\rangle$	10 / −15	6 / 9	0 / 6	0 / 36	24 / 36	0 / 48
$\langle c''_{112}\rangle = \langle c''_{122}\rangle$	2 / −3	14 / −11	0 / 14	0 / 20	−8 / 20	0 / −16
$\langle c''_{113}\rangle = \langle c''_{223}\rangle$	0 / 6	12 / 2	4 / −8	8 / −32	0 / −8	0 / −32
$\langle c''_{123}\rangle$	0 / 2	4 / 22	12 / −24	−8 / −32	0 / −24	0 / 32
$\langle c''_{133}\rangle = \langle c''_{233}\rangle$	0 / 8	16 / −24	0 / 16	0 / 32	0 / −32	0 / 0
$\langle c''_{144}\rangle$	0 / 2	0 / 10	0 / −12	12 / −20	4 / −12	−8 / 8
$\langle c''_{155}\rangle = \langle c''_{244}\rangle$	0 / 6	0 / −2	0 / −4	4 / −28	12 / −4	8 / −40
$\langle c''_{166}\rangle = \langle c''_{266}\rangle$	2 / −3	−2 / 5	0 / −2	0 / 4	8 / 4	0 / 16
$\langle c''_{255}\rangle$	0 / 2	0 / 10	0 / −12	12 / −20	4 / −12	−8 / 8
$\langle c''_{333}\rangle$	16 / −48	0 / 48	0 / 0	0 / 0	0 / 192	0 / 0
$\langle c''_{344}\rangle = \langle c''_{355}\rangle$	0 / 8	0 / −8	0 / 0	0 / 16	16 / −48	0 / 32
$\langle c''_{366}\rangle$	0 / 2	4 / −10	−4 / 8	8 / 0	0 / 8	0 / −32
$\langle c''_{456}\rangle$	0 / 2	0 / −6	0 / 4	−4 / −4	4 / 4	8 / −24

Table 46
Linear pyroelectric coefficients (p_j) referred to the unrotated crystal axes.

System →	Triclinic	Monoclinic		Rhombic	Tetragonal		Trigonal		Hexagonal	
Laue →	I		II	III	IVa	IVb	Va	Vb	VIa	VIb
H-M →	1	2	m	$mm2$	4	$4mm$	3	$3m$	6	$6mm$
	Pyroelectric matrix									
	p_1	0	p_1			0				
	p_2	p_2	0			0				
	p_3	0	p_3			p_3				

Table 47
Averaged linear pyroelectric coefficients for both x_1 and x_2 rotations.

The averaged $\langle p_1\rangle$ and $\langle p_2\rangle$ coefficients vanish identically: $\langle p_1\rangle = \langle p_2\rangle \equiv 0$.

System →	Triclinic	Monoclinic		Rhombic	Tetragonal		Trigonal		Hexagonal	
Laue →	I		II	III	IVa	IVb	Va	Vb	VIa	VIb
H-M →	1	2	m	$mm2$	4	$4mm$	3	$3m$	6	$6mm$
Rotation					$\langle p_3\rangle$					
x_1	$-p_2S$ $+p_3C$	$-p_2S$	0			$+p_3C$				
x_2	$+p_1S$ $+p_3C$	0	$+p_1S$ $+p_3C$			$+p_3C$				

1984; Lang, 2005), although TGS still remains the material of choice for many thermal applications such as in sensors / detectors (temperature measurement, UV/IR detection, motion sensing, spectrometry), energy harvesters, and particularly in thermal imagers (medical diagnostics, building inspection, surveillance) (Velarde *et al.*, 2021).

The pyroelectric vector arrays are given in Table 46 for the ten crystal classes in which this effect can exist. Table 47 displays the results resulting from the averaging procedure, for both x_1 and x_2 rotations. It is worth noting that these results are identical for the electrocaloric effect (Forsbergh, 1956; Newnham, 2005) and for the pyromagnetic effect (Chynoweth, 1958).

6. Conclusions

The rotating substrate method of crystallite deposition applied in the prequel to linear material coefficients of ranks 2, 3 and 4, has been extended to certain nonlinear effects characterized by coefficients of ranks 3, 4, 5 and 6. These include general triclinic versions of dielectric, piezoelectric, and elastic effects, as well as linear, rank 1, pyroelectricity.

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