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The piezoelectric effect of second order in stress or strain: its form for crystals and quasicrystals of any symmetry

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The restrictions on the coefficients describing physical effects depend on the orientation of the symmetry elements of the crystal or quasicrystal with respect to the Cartesian coordinate system employed. They are given for the piezoelectric effect of second order in stress or strain for all the orientations that can be expressed by the sequence of elements in the Hermann–Mauguin symbol of the point group. In the literature, the restrictions are usually given only for a particular orientation, which sometimes is not specified.

1. Introduction

Piezoelectric effects of higher order have aroused much interest in view of technical applications. Piezoelectric effects of second order in stress or strain have been determined experimentally, *e.g.* in α-quartz (Kittinger *et al.*, 1986), in lithium niobate (Cho & Yamanouchi, 1987), in potassium niobate (Cho *et al.*, 2000) or using density-functional theory in III–V semiconductors (Bester *et al.*, 2006). All these materials have different point-group symmetries, 32, 3*m*, *mm*2 and $\bar{4}3m$, respectively. The restrictions on the coefficients describing the piezoelectric effect depend on the orientation of the symmetry elements of the crystal or quasicrystal with respect to the Cartesian coordinate system, which is normally used in crystal physics. Koptsik (1966) was first to determine the form of the piezoelectric effects of second order in *stress* for the 21 non-centrosymmetric crystallographic point groups in a particular orientation. Later, Nelson (1979) determined the form of the piezoelectric effects of second order in *strain* for the same point groups, not always in the same orientation. Unfortunately, the results of both authors contain a number of errors. In the present paper, these errors are corrected and the results extended to all the standard orientations that can be expressed by a particular sequence of symmetry elements in the Hermann–Mauguin symbol of the point group. Recently, the results have been extended to a number of quasicrystal point groups by Rama Mohana Rao *et al.* (2007). They claim that the coefficients in their Table 2 give the electric polarization as a function of the stresses, whereas they give it as a function of the strains. Their results are extended to all quasicrystal point groups in all standard orientations. In the present paper, all results will be given for the stresses as well as for the strains and presented in the lucid notation of Nye (1985).

2. The form of the matrix describing the piezoelectric effect of second order in stress or strain

The electric polarization P_i as a function of mechanical stress σ_{jk} can be written as

$$P_i = d_{ijk}\sigma_{jk} + D_{ijklm}\sigma_{jk}\sigma_{lm}. \tag{1}$$

Koptsik (1966) considered the contribution of second order D_{ijklm}. The tensor σ_{jk} being symmetric in j and k has six independent components that are usually referred to as

$$\sigma_1 = \sigma_{11},\ \sigma_2 = \sigma_{22},\ \sigma_3 = \sigma_{33},\ \sigma_4 = \sigma_{23},\ \sigma_5 = \sigma_{31},\ \sigma_6 = \sigma_{12}. \tag{2}$$

Equation (1) can then be written as

$$P_i = d_{i\mu}\sigma_\mu + D_{i\mu\nu}\sigma_\mu\sigma_\nu, \tag{3}$$

where Greek indices run from 1 to 6. In order to preserve the usual rules of summing over repeated indices, we must define

$$\begin{aligned} d_{i1} &= d_{i11},\ d_{i2} = d_{i22},\ d_{i3} = d_{i33}, \\ d_{i4} &= 2d_{i23},\ d_{i5} = 2d_{i31},\ d_{i6} = 2d_{i12} \end{aligned} \tag{4}$$

and, analogously,

$$\begin{aligned} D_{i\mu\nu} &= D_{ijklm} && \text{if } \mu, \nu = 1, 2, 3, \\ D_{i\mu\nu} &= 2D_{ijklm} && \text{if only one of } \mu, \nu = 1, 2, 3, \\ D_{i\mu\nu} &= 4D_{ijklm} && \text{if } \mu, \nu = 4, 5, 6. \end{aligned} \tag{5}$$

[Koptsik (1966) uses wrong powers of 2 if $\mu \neq \nu$.]

The electric polarization P_i as a function of mechanical strain ε_{jk} can be written as

$$P_i = e_{ijk}\varepsilon_{jk} + E_{ijklm}\varepsilon_{jk}\varepsilon_{lm}. \tag{6}$$

The tensor ε_{jk} being symmetric in j and k has six independent components that are usually referred to as

$$\varepsilon_1 = \varepsilon_{11},\ \varepsilon_2 = \varepsilon_{22},\ \varepsilon_3 = \varepsilon_{33},\ \varepsilon_4 = 2\varepsilon_{23},\ \varepsilon_5 = 2\varepsilon_{31},\ \varepsilon_6 = 2\varepsilon_{12}. \tag{7}$$

Equation (6) can then be written as

$$P_i = e_{i\mu}\varepsilon_\mu + E_{i\mu\nu}\varepsilon_\mu\varepsilon_\nu. \tag{8}$$

It follows that

$$e_{i\mu} = e_{ijk} \quad \text{if } \mu = 1, 2, \ldots, 6 \tag{9}$$

and

$$E_{i\mu\nu} = E_{ijklm} \quad \text{if } \mu, \nu = 1, 2, \ldots, 6. \tag{10}$$

The Hermann–Mauguin symbols (HMS) can be interpreted as giving symmetry elements of point groups in a specified orientation with respect to the axes x, y and z of the Cartesian coordinate system used for describing the physical property under consideration. For the orthorhombic groups, x is parallel to the first entry in the HMS, y parallel to the second and z parallel to the third. If, in the monoclinic case, one wants to indicate the choice of the monoclinic axis, symbols with three entries can be used as in the orthorhombic case, *e.g.* 121 indicates a rotation axis $2 \parallel y$, $11m$ a mirror plane $m \perp z$. In the cases (crystallographic or not) with a principal axis n or $\bar{n}$, $n \geq 3$, the principal symmetry direction given by the first entry is parallel to z, whereas one of the secondary symmetry directions given by the second entry is parallel to x (and another parallel to y for n with n even or $\bar{n}$ with $n/2$ even). If n is odd, symbols with three entries can be used to indicate whether a secondary axis is along x or y, *e.g.* $3m1$ indicates a mirror plane $m \perp x$, 312 a rotation axis $2 \parallel y$. Finally, in the cubic and icosahedral cases, symmetry elements given by the first entry appear along x, y and z.

These conventions are stressed here because often the orientation with respect to the Cartesian coordinate system is not indicated in the literature, leading to confusion. Examples: the form that Nelson (1979) gives in Table 9 of the Appendix for $E_{i\mu\nu}$ under the heading $\bar{6}m2$ is valid for $2 \parallel x$, *i.e.* for $\bar{6}2m$; the form that Rama Mohana Rao *et al.* (2007) give under the headings $5m$ and $\overline{10}m2$ are valid for $m \perp y$, *i.e.* for $51m$ and $\overline{10}2m$.

The tensors D_{ijklm} and E_{ijklm} are symmetric under an interchange of jk and lm. It follows that $D_{i\mu\nu}$ and $E_{i\mu\nu}$ are symmetric under an interchange of μ and ν; they can be characterized by matrices with three rows corresponding to $i = 1, 2, 3$, and 21 columns corresponding to $\mu, \nu = 1, 2, \ldots, 6$ with $\mu \leq \nu$. The 21 columns will be arranged such that coefficients that are equal or multiples of each other [which in Nye notation (Nye, 1985) are connected by a line] do not lie too far apart. The same order of the 21 columns will be used for all point groups.

As explained *e.g.* in Bhagavantam (1966), it follows from Neumann's principle that D_{ijklm} and E_{ijklm}, being polar tensors of odd rank, vanish for the centrosymmetric point groups. In addition, these tensors vanish also for the icosahedral point group 235 and the dodecagonal point groups $\overline{12}$, $\overline{12}2m$ and $\overline{12}m2$. The non-vanishing forms of the 3×21 matrices for the point groups of crystals and quasicrystals are given in Nye notation (the notation being explained in Fig. 1) in Figs. 2–9.

The forms of D_{ijklm} and E_{ijklm} have been determined using the direct inspection method of Fumi (1952*a*,*b*) in the cases where the point-group symmetry contains only rotations, and using results by Grimmer (1991, 2007) in the other non-centrosymmetric cases. Consider a change of the Cartesian coordinate system such that the vector $\mathbf{v}$ has components v_i in the old system and $v'_i = a_{ij}v_j$ in the new one. The components of D_{ijklm} in the new system are then

$$D'_{ijklm} = a_{ip}a_{jq}a_{kr}a_{ls}a_{mt}D_{pqrst} \tag{11}$$

and similarly for E_{ijklm}. If the change of the coordinate system corresponds to a point-group symmetry operation of the material under consideration, the tensor will have the same components in the primed and the unprimed system according to the Neumann principle. Consider as an example the monoclinic point group 211: it is generated by the 180° rotation about x, for which

$$a_{ij}(2_x) = \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix}.$$

It follows that $D'_{ijklm} = D_{ijklm}$ if an even number of the five indices i,

	$D_{i\mu\nu}$	$E_{i\mu\nu}$
·	zero component	zero component
●	non-zero component	non-zero component
a	$D_{111} = -(D_{122} + 2D_{112})$	$E_{111} = -(E_{122} + 2E_{112})$
b	$D_{126} = -(D_{222} + 3D_{212})$	$E_{126} = -\frac{1}{2}(E_{222} + 3E_{212})$
c	$D_{116} = -(D_{222} - D_{212})$	$E_{116} = -\frac{1}{2}(E_{222} - E_{212})$
d	$D_{146} = D_{115} - D_{125}$	$E_{146} = \frac{1}{2}(E_{115} - E_{125})$
e	$D_{156} = D_{124} - D_{114}$	$E_{156} = \frac{1}{2}(E_{124} - E_{114})$
f	$D_{211} = -\frac{1}{2}(D_{222} + 2D_{212})$	$E_{211} = -\frac{1}{2}(E_{222} + 2E_{212})$
g	$D_{226} = D_{122} + 3D_{112}$	$E_{226} = \frac{1}{2}(E_{122} + 3E_{112})$
h	$D_{216} = D_{122} - D_{112}$	$E_{216} = \frac{1}{2}(E_{122} - E_{112})$
i	$D_{366} = 2(D_{311} - D_{312})$	$E_{366} = \frac{1}{2}(E_{311} - E_{312})$
Components that are multiples of each other are joined by a line. Note that in some cases of Figures 4-9 lines will cross or cover points marking zero components. (j stands for any of the letters a, b, ... , i):		
●—● , j—●	equal components	equal components
●—◐ , j—◐	2 times the component on the left	
●—■ , j—■	4 times the component on the left	
●—○ , j—○	-1 times the component on the left	components numerically equal but opposite in sign
●—◯ , j—◯	-2 times the component on the left	
●—□ , j—□	-4 times the component on the left	

Figure 1
Explanation of the symbols used in Figs. 2–9.

j, k, l, m are 2 or 3, *i.e.* if an odd number equal 1, and that $D'_{ijklm} = -D_{ijklm}$ if an even number of these five indices equal 1. In the second case, D_{ijklm} must vanish, whereas in the first it may have any value. Considering how an index μ is related to a pair i, j, one finds that $D_{i\mu\nu}$ (and $E_{i\mu\nu}$) must have the form $F(211)$ given in Fig. 2.

In what follows, use will be made of the following operations: $F(C) = F(A) \oplus F(B)$ means that each matrix F satisfying the restrictions C can uniquely be written as the sum of a matrix satisfying the restrictions A and a matrix satisfying the restrictions B. The same will be expressed also as $F(A) = F(C) \ominus F(B)$ or as $F(B) = F(C) \ominus F(A)$. $F(D) = F(A) \cap F(B)$ means that each matrix F satisfying the restrictions D satisfies the restrictions A and the restrictions B.

Because 211 and $m11$ have only the identity 1 in common, and together they generate $2/m11$, *i.e.* a centrosymmetric group, any matrix $F(1)$ can be written uniquely as a sum of a matrix satisfying the restrictions for 211 and a matrix satisfying the restrictions for $m11$: $F(1) = F(211) \oplus F(m11)$. The restrictions for $F(m11)$ can therefore be obtained as $F(m11) =$

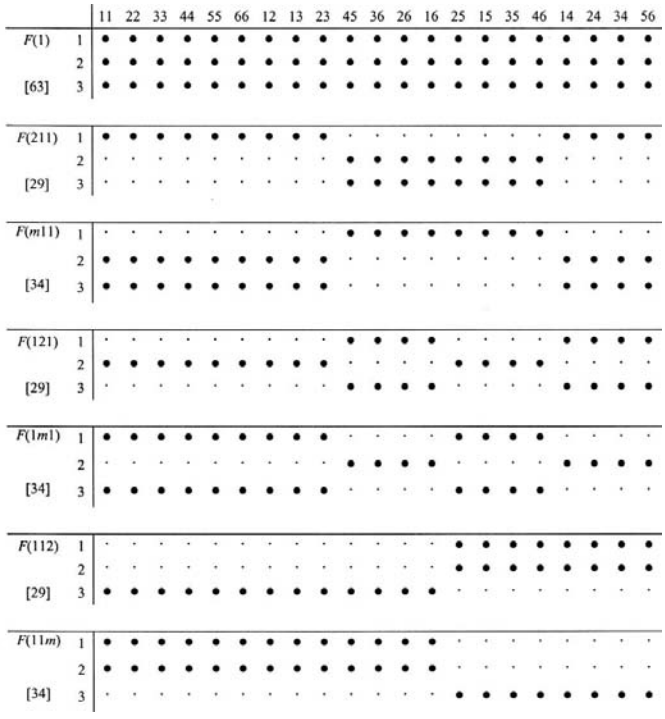

Figure 2
Forms of $D_{i\mu\nu}$ and $E_{i\mu\nu}$ for the non-centrosymmetric triclinic and monoclinic point groups. Numbers between brackets indicate the number of independent components.

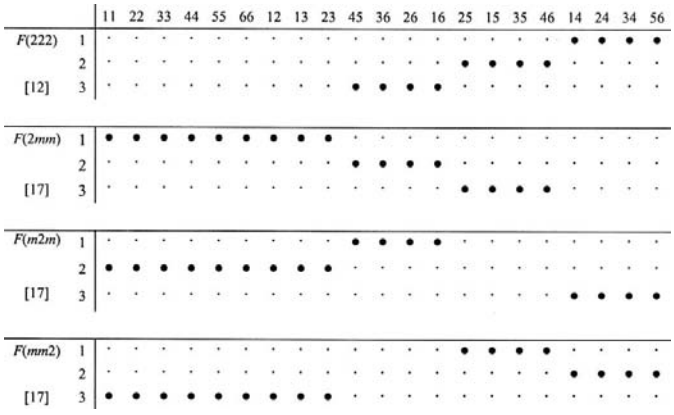

Figure 3
Forms of $D_{i\mu\nu}$ and $E_{i\mu\nu}$ for the non-centrosymmetric orthorhombic point groups. Numbers between brackets indicate the number of independent components.

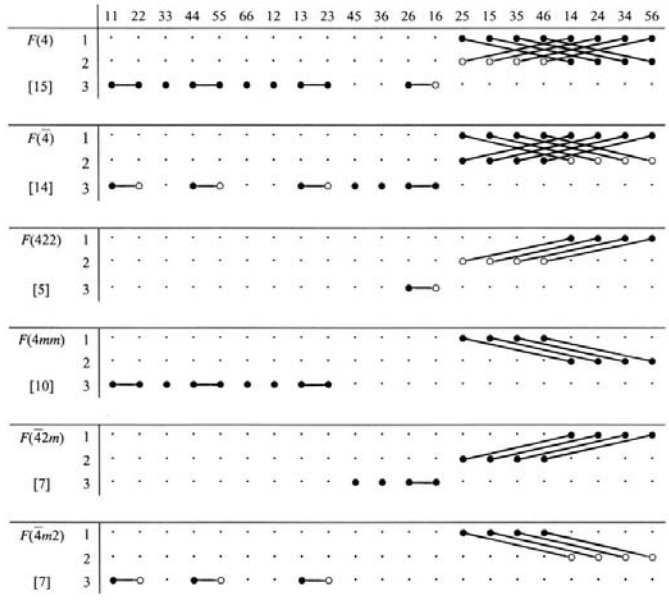

Figure 4
Forms of $D_{i\mu\nu}$ and $E_{i\mu\nu}$ for the non-centrosymmetric tetragonal point groups. Numbers between brackets indicate the number of independent components.

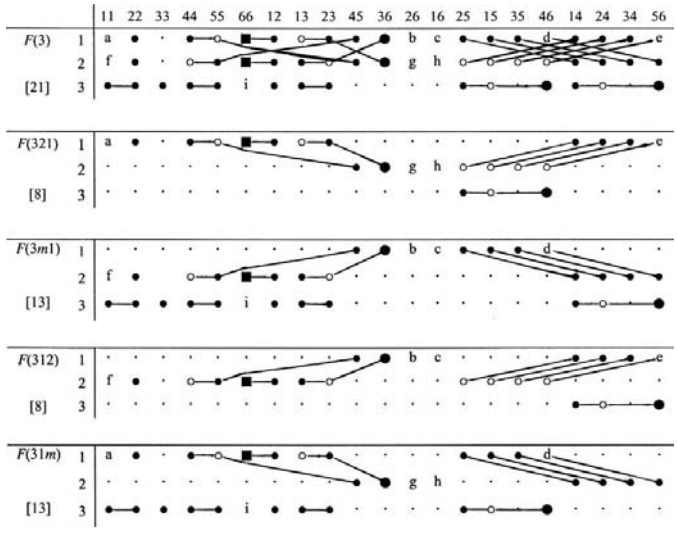

Figure 5
Forms of $D_{i\mu\nu}$ and $E_{i\mu\nu}$ for the non-centrosymmetric trigonal point groups. Numbers between brackets indicate the number of independent components.

$F(1) \ominus F(211)$, see Fig. 2. Similar considerations lead to the forms $F(121)$ and $F(112)$, from which $F(1m1) = F(1) \ominus F(121)$ and $F(11m) = F(1) \ominus F(112)$ are obtained.

The orthorhombic symmetry 222 is generated by 211 and 121. The form $F(222)$ therefore satisfies the restrictions for 211 and 121: $F(222) = F(211) \cap F(121)$, similarly $F(2mm) = F(211) \cap F(1m1)$, $F(m2m) = F(m11) \cap F(121)$, $F(mm2) = F(m11) \cap F(1m1)$, see Fig. 3.

The tetragonal form $F(4)$ is a special case of $F(112)$ because 112 ($= 2_z$) is a subgroup of 4 ($= 4_z$). For a 90° rotation about z, the transformation matrix has the form

$$a_{ij}(4_z) = \begin{pmatrix} 0 & -1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix}.$$

The requirement of invariance leads to the form $F(4)$ given at the top of Fig. 4. The remaining forms in Fig. 4 follow easily as follows: $F(422) = F(4) \cap F(222)$. Because 422 and 4$mm$ have 4 in common, and together generate the centrosymmetric group 4/mmm, any matrix satisfying the restrictions for 4 can be written uniquely as a sum of a matrix satisfying the restrictions for 422 and a matrix satisfying the restrictions for 4mm: $F[4] = F[422] \oplus F[4mm]$. The restrictions for $F[4mm]$ can therefore be obtained as $F[4mm] = F[4] \ominus F[422]$. Similarly, 4 and $\bar{4}$ have 2 in common, together they generate the centrosymmetric group 4/m. It follows that $F[\bar{4}] = F[2] \ominus F[4]$. Analogously, $F[\bar{4}2m] = F[222] \ominus F[422]$, $F[\bar{4}m2] = F[mm2] \ominus F[4mm]$.

For a 120° rotation about z, the transformation matrix has the form

$$a_{ij}(3_z) = \begin{pmatrix} -1/2 & -\sqrt{3}/2 & 0 \\ \sqrt{3}/2 & -1/2 & 0 \\ 0 & 0 & 1 \end{pmatrix},$$

which leads to more complicated results, which have been published by Koptsik (1966) for D and by Nelson (1979) for E. I checked their results using (11). Whereas Nelson (1979) is correct, there remains an error in Koptsik (1966) (even after correcting for the wrong power of 2 if $\mu \neq \nu$), who states that D_{322} vanishes whereas $D_{322} = D_{311}$. Once $F(3)$ has been determined, all the other trigonal and hexagonal forms follow easily: $F(321) = F(3) \cap F(211)$, $F(312) = F(3) \cap F(121)$, $F(3m1) = F(3) \ominus F(321)$, $F(31m) = F(3) \ominus F(312)$. $F(6) = F(3) \cap F(112)$, $F(\bar{6}) = F(3) \ominus F(6)$, $F(622) = F(6) \cap F(211)$, $F(6mm) = F(6) \ominus F(622)$, $F(\bar{6}2m) = F(321) \ominus F(622)$, $F(\bar{6}m2) = F(3m1) \ominus F(6mm)$.

The cubic group 23 may be generated by 222 and a 120° rotation about the sum of the three basis vectors of the Cartesian coordinate system. $F(23)$ is therefore a special case of $F(222)$, which is given in Fig. 7. $F(432) = F(23) \cap F(4)$, $F(\bar{4}3m) = F(23) \ominus F(432)$.

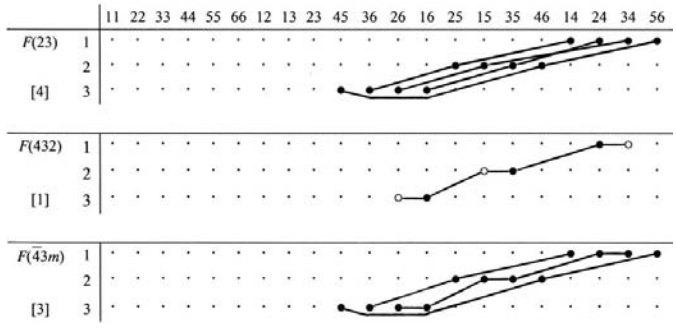

Figure 7
Forms of $D_{i\mu\nu}$ and $E_{i\mu\nu}$ for the non-centrosymmetric cubic point groups. Numbers between brackets indicate the number of independent components.

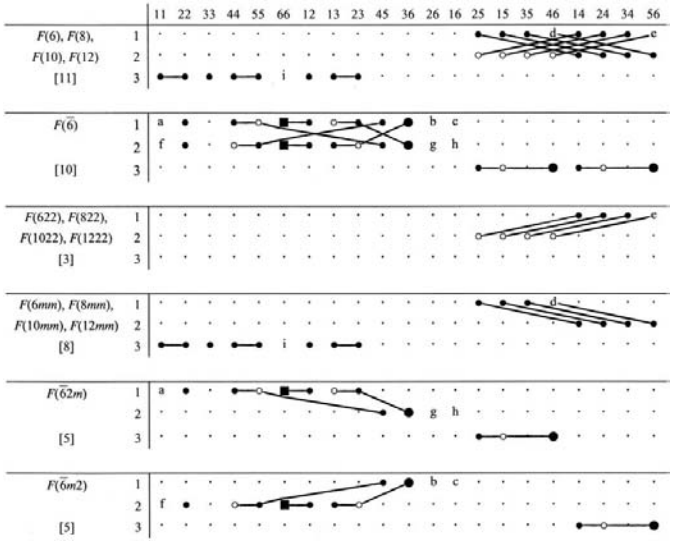

Figure 6
Forms of $D_{i\mu\nu}$ and $E_{i\mu\nu}$ for the non-centrosymmetric hexagonal and some octagonal, decagonal and dodecagonal point groups. Numbers between brackets indicate the number of independent components.

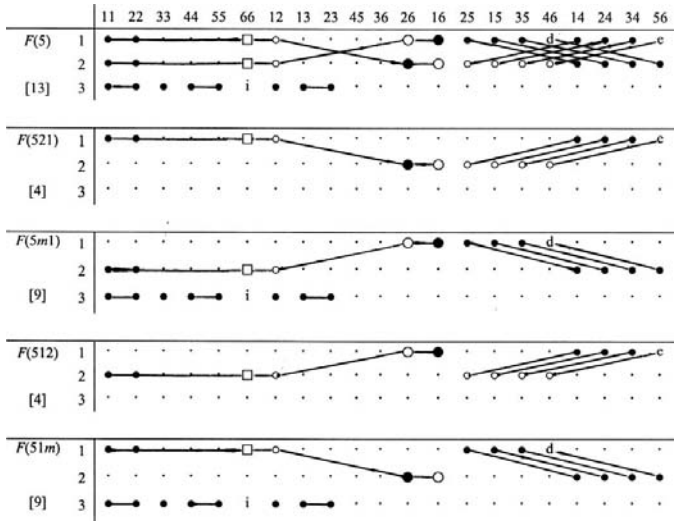

Figure 8
Forms of $D_{i\mu\nu}$ and $E_{i\mu\nu}$ for the non-centrosymmetric pentagonal point groups. Numbers between brackets indicate the number of independent components.

For a 72° rotation about z, the transformation matrix has the form

$$a_{ij}(5_z) = \begin{pmatrix} (\sqrt{5}-1)/4 & -\sqrt{(5+\sqrt{5})/8} & 0 \\ \sqrt{(5+\sqrt{5})/8} & (\sqrt{5}-1)/4 & 0 \\ 0 & 0 & 1 \end{pmatrix},$$

which again leads to a rather complicated result, which has been published by Rama Mohana Rao *et al.* (2007) for D. I checked their result using (11) and found that it holds for E, not for D. Once $F(5)$ has been determined, all the other pentagonal forms follow easily: $F(521) = F(5) \cap F(211)$, $F(512) = F(5) \cap F(121)$, $F(5m1) = F(5) \ominus F(521)$, $F(51m) = F(5) \ominus F(512)$, see Fig. 8. Also the octagonal, decagonal and dodecagonal forms are easily obtained thanks to a theorem of Hermann (1934), which states that invariance under an n-fold rotation has the same effect as invariance under an ∞-fold rotation for tensors of rank $< n$. It follows that $F(8) = F(10) = F(12) = F(6)$, $F(822) = F(1022) = F(1222) = F(622)$, $F(8mm) = F(10mm) = F(12mm) = F(6mm)$, see Fig. 6. Notice that the subgroup of rotations in $\bar{n}$ with n even is only $n/2$. $F(\bar{8}) = F(4) \ominus F(8)$, $F(\bar{8}2m) = F(422) \ominus F(822)$, $F(\bar{8}m2) = F(4mm) \ominus F(8mm)$; $F(\overline{10}) = F(5) \ominus F(10)$, $F(\overline{10}2m) = F(521) \ominus F(1022)$, $F(\overline{10}m2) = F(5m1) \ominus F(10mm)$; $F(\overline{12}) = F(6) \ominus F(12) = 0$, $F(\overline{12}2m) = F(622) \ominus F(1222) = 0$, $F(\overline{12}m2) = F(6mm) \ominus F(12mm) = 0$. The non-vanishing forms with an axis $\bar{n}$, $n = 8$, 10 or 12, are given in Fig. 9.

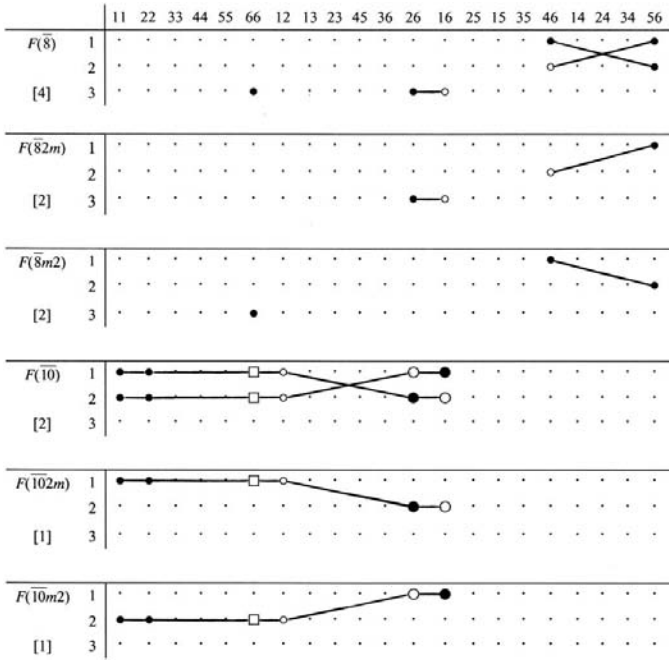

Figure 9
Forms of $D_{i\mu\nu}$ and $E_{i\mu\nu}$ for octagonal and decagonal point groups with axis 8 and 10, respectively. Numbers between brackets indicate the number of independent components. The forms $D_{i\mu\nu}$ and $E_{i\mu\nu}$ vanish for the dodecagonal point groups $\overline{12}$, $\overline{12}2m$ and $\overline{12}m2$.

3. Discussion

The notation used in this paper has the advantage of showing immediately which matrix elements are equal or multiples of each other. The results have been given not only for $E_{i\mu\nu}$ but also for $D_{i\mu\nu}$, *i.e.* not only for the piezoelectric effect as a function of strain but also as a function of stress. Figs. 1–4 and 7 show for triclinic, monoclinic, orthorhombic, tetragonal and cubic point groups that the same restrictions follow from the Neumann principle on the forms of $D_{i\mu\nu}$ and $E_{i\mu\nu}$.

The forms of $D_{i\mu\nu}$ and $E_{i\mu\nu}$ have been given for all orientations in which the point groups appear in the standard orientation of the corresponding holohedry; in the monoclinic case, all three settings have been considered. The latter was needed for an easy derivation of forms for higher symmetries. In addition, it is often convenient to consider point groups not only in the standard orientation with respect to the Cartesian coordinate system, especially in connection with phase transition, *e.g.* when the high-temperature phase with symmetry $4/mmm$ splits into two domains with the oriented symmetries $\bar{4}2m$ and $\bar{4}m2$. Notice that the forms $F(\bar{4}2m)$ and $F(\bar{4}m2)$, given in Fig. 4, look very different. Often authors do not make clear which orientation they consider, which may lead to confusion: the form given by Nelson (1979) for $\bar{6}m2$ really corresponds to $\bar{6}2m$ (= $\bar{6}_z 2_x m$); the form that Rama Mohana Rao *et al.* (2007) give for $5m$ really corresponds to $51m$ (= $5_z 1 m_y$), their form for $\overline{10}m2$ really corresponds to $\overline{10}2m$ (= $\overline{10}_z 2_x m$).

We noted a few other mistakes in the often used Table 9 of Nelson (1979): E_{345} need not vanish for $\bar{4}$; it may have any value W, as for $\bar{4}2m$. $D \cong -(A + 2B)$ for $3m$, not $D \cong -(A - 2B)$. The first hexagonal form holds for 6 not for $\bar{6}$.

Rama Mohana Rao *et al.* (2007) do not consider the symmetries of octagonal and dodecagonal quasicrystals and only two of the decagonal symmetries; we added the missing cases. Notice that $D_{i\mu\nu}$ and $E_{i\mu\nu}$ vanish also for the only non-centrosymmetric icosahedral point group 235, as follows from equation (2.2) of Rama Mohana Rao *et al.* (2007). The forms derived applying the Neumann principle to the quasicrystal symmetries hold for the phonon part of the tensor, as discussed in Grimmer (2007).

It has been shown that, once the results are known for 2_x, 2_y, 2_z, 3_z, 3_{xxx}, 4_z and 5_z, it is easy to write them down for all the cases that we considered. Notice that the forms 3_z and 5_z are rather closely related: the same combinations d, e and i that appear in $F(5)$ appear also in $F(3)$ in the same positions.

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