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X-ray Determination of Piezoelectric Constants*

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The theoretical equations required for the experimental determination of the complete set of piezoelectric constants from X-ray measurements are presented. For this purpose the expression for the quantity ($\partial\theta/\partial E$), where θ denotes the Bragg angle and E the magnitude of an applied electric field is calculated as a function of the field direction and the reflecting lattice plane normal. For all 20 crystal classes exhibiting the piezoelectric effect explicit expressions are given for the longitudinal and transverse piezoelectric effect, corresponding to parallel-field and perpendicular-field reflection, respectively. For the 19 piezoelectric classes of the monoclinic, orthorhombic, tetragonal, trigonal, hexagonal and cubic systems explicit expressions for ($\partial\theta/\partial E$) in terms of the Miller indices of the reflecting planes are given for the simplest crystal cuts with respect to the symmetry elements present. The use of the equations is illustrated by a numerical example dealing with a crystal of symmetry *mm*2.

Introduction

It has been shown by Bhalla, Bose, White & Cross (1971) that piezoelectric constants may be determined directly by using X-rays to measure the elastic strain induced in a piezoelectric crystal by a static electric field. By this method these authors have measured the piezoelectric constant d_{11} of α-quartz and found good agreement with earlier data obtained with other methods. As pointed out by Bhalla, Bose, White & Cross (1971), the X-ray method has several advantages over other methods. Among these are its ready applicability to small crystals (about $1\times1\times0{\cdot}1$ mm) and the possibility to distinguish spontaneous and induced strains in ferroelectric crystals and to determine the piezoelectric constants of individual domains. In addition, the X-ray method avoids some of the potential difficulties associated with other methods, such as the occurrence of mode coupling in the widely used resonance–antiresonance method (see, *e.g.*, Mason, 1950).

It is the purpose of the present paper to present the theoretical equations for the X-ray determination of the complete set of the piezoelectric constants for crystals of all twenty crystal classes which exhibit the piezoelectric effect.

Theoretical derivation

Bragg's form of the condition for constructive reflection of an incident X-ray beam by a lattice plane with Miller indices *hkl* and interplanar spacing d_{hkl} is given by

$$\sin\theta=\frac{n\lambda}{2d_{hkl}}\,, \tag{1}$$

where

$$\frac{1}{d_{hkl}}=G_{hkl}=(\mathbf{G}_{hkl}\,.\,\mathbf{G}_{hkl})^{1/2} \tag{2}$$

and

$$\mathbf{G}_{hkl}=h\mathbf{a}^*+k\mathbf{b}^*+l\mathbf{c}^* \tag{3}$$

denotes a reciprocal lattice vector. $\mathbf{a}^*,\mathbf{b}^*,\mathbf{c}^*$ are the base vectors of the reciprocal lattice defined by $\mathbf{a}\,.\,\mathbf{a}^*=1$, $\mathbf{a}\,.\,\mathbf{b}^*=0$, *etc.*, where $\mathbf{a},\mathbf{b},\mathbf{c}$ are the unit-cell vectors of the direct space lattice. If, as in equation (1), the order of the reflection appears explicitly the Miller indices must be assumed to consist of coprime integers (*i.e.* of integers without a common factor except unity).

By applying an electric field $\mathbf{E}$ with components $E_r=E\alpha_r$ (α_r being the direction cosines, and $r=1,2,3$ denotes three Cartesian coordinate axes) to a crystal, an elastic strain $\varepsilon_{ij}(i,j=1,2,3)$ is induced through the converse piezoelectric effect according to (Nye, 1957)

$$\varepsilon_{ij}=d_{rij}E_r\,, \tag{4}$$

d_{rij} denotes the third-rank tensor of the piezoelectric strain constants, and the summation convention is used here and subsequently (*i.e.* summation over the three values 1,2,3 is implied for every pair of identical indices). Of course, the components E_r of the electric field $\mathbf{E}$ and of the strain tensor ε_{ij}, and the set of piezoelectric constants d_{rij} must be referred to a common Cartesian coordinate system with axes, x_1,x_2,x_3.

In order to obtain the dependence of the reciprocal interplanar distance d_{hkl}^{-1} on strain ε_{ij}, consider the matrices A and A* composed of the unit-cell vectors of the direct and reciprocal lattices, respectively, according to

$$\mathsf{A}=\begin{pmatrix}a_1b_1c_1\\a_2b_2c_2\\a_3b_3c_3\end{pmatrix}\,,\quad \mathsf{A}^*=\begin{pmatrix}a_1^*b_1^*c_1^*\\a_2^*b_2^*c_2^*\\a_3^*b_3^*c_3^*\end{pmatrix}\,. \tag{5}$$

The relations $\mathbf{a}\,.\,\mathbf{a}^*=1$, $\mathbf{a}\,.\,\mathbf{b}^*=0$, *etc.* can then be

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written in matrix notation as

$$\mathsf{A}\mathsf{A}^{*T}=\mathsf{A}^{T}\mathsf{A}^{*}=\mathsf{I}\,, \tag{6}$$

where the superscript T denotes the transpose matrix, and I the unit matrix.

In the approximation of the linear theory of elasticity under the influence of a strain $\boldsymbol{\varepsilon}$ the base vectors change according to $\mathbf{a}(\boldsymbol{\varepsilon})=(\mathsf{I}+\boldsymbol{\varepsilon})\mathbf{a}(0)$, *etc.*, where $\boldsymbol{\varepsilon}$ denotes the strain tensor ε_{ij} in matrix notation. Therefore, the direct and reciprocal base vector matrices change according to

$$\mathsf{A}(\boldsymbol{\varepsilon})\;=(\mathsf{I}+\boldsymbol{\varepsilon})\mathsf{A}(\mathbf{0}) \tag{7a}$$

$$\mathsf{A}^{*}(\boldsymbol{\varepsilon})=(\mathsf{I}+\boldsymbol{\varepsilon})^{-1}\mathsf{A}^{*}(\mathbf{0})\simeq(\mathsf{I}-\boldsymbol{\varepsilon})\mathsf{A}^{*}(\mathbf{0})\,. \tag{7b}$$

In the spirit of the linear theory of elasticity, higher than first powers of $\boldsymbol{\varepsilon}$ have been neglected in the last step of equation (*7b*).

According to (*7b*) a reciprocal lattice vector $\mathbf{G}_{hkl}$ changes according to

$$\mathbf{G}_{hkl}(\boldsymbol{\varepsilon})=(\mathsf{I}-\boldsymbol{\varepsilon})\mathbf{G}_{hkl}(\mathbf{0})\,. \tag{8}$$

Therefore,

$$\mathbf{G}_{hkl}(\boldsymbol{\varepsilon})\,.\,\mathbf{G}_{hkl}(\boldsymbol{\varepsilon})=\mathbf{G}_{hkl}(\mathbf{0})\,.\,\mathbf{G}_{hkl}(\mathbf{0})-2[\mathbf{G}_{hkl}(\mathbf{0})\,.\,\boldsymbol{\varepsilon}\mathbf{G}_{hkl}(\mathbf{0})] \tag{9}$$

and

$$G_{hkl}(\varepsilon)=G_{hkl}(0)[1-(\mathbf{N}\,.\,\boldsymbol{\varepsilon}\mathbf{N})]\,, \tag{10}$$

where

$$\mathbf{N}=\frac{\mathbf{G}_{hkl}}{G_{hkl}} \tag{11}$$

denotes the normal of the lattice plane (hkl).

In view of equations (1), (2), (4) and (10) the diffraction angle θ depends on the magnitude E of the electric field, $\theta=\theta[\boldsymbol{\varepsilon}(E)]$, so that one obtains by differentiation (summation convention!)

$$\left(\frac{\partial\ln\sin\theta}{\partial E}\right)=\left(\frac{\partial\ln G_{hkl}}{\partial\varepsilon_{ij}}\right)\left(\frac{\partial\varepsilon_{ij}}{\partial E_{r}}\right)\left(\frac{\partial E_{r}}{\partial E}\right),$$

or

$$\cot\theta\left(\frac{\partial\theta}{\partial E}\right)=-\alpha_{r}N_{i}N_{j}d_{rij}\,. \tag{12}$$

This relation is the generalized form of equation (6) of the paper by Bhalla, Bose, White & Cross (1971). For the special case that both the direction of the electric field and the reflecting lattice plane normal are in the x_1 direction, $\alpha_r=\delta_{1r}$, $N_i=\delta_{1i}$, $N_j=\delta_{1j}$ (δ_{mn} denotes the Kronecker symbol, *i.e.* $\delta_{mn}=1$ for $m=n=1,2,3$, and $\delta_{mn}=0$ for $m\neq n$), equation (12) becomes equivalent to equation (6) of these authors.

Equation (12) provides the theoretical basis for the experimental determination of the complete set of piezoelectric constants of any piezoelectric material. In order to determine the complete set of piezoelectric constants the dependence of the reflection angle θ on the magnitude of the electric field must be measured for a set of combinations of directions $\boldsymbol{\alpha},\mathbf{N}$ equal in number to, or if redundancy checks are desired, larger than the number of independent piezoelectric constants corresponding to the crystal class of the material under investigation.

In order to eliminate electrostriction the measurements should be carried out with field reversal which changes the sign of equation (12), but not of the quadratic electrostriction effect.

Application of the electric field requires a set of thin platelets of the piezoelectric materials with plane parallel electroded faces, so that the direction of one of the two face normals of opposite directions coincides with the direction of $\boldsymbol{\alpha}=(\alpha_1\alpha_2\alpha_3)$ of the electric field. In practice, the direction of the reflecting lattice planes is restricted to the two cases $\mathbf{N}\|\boldsymbol{\alpha}$ and $\mathbf{N}\perp\boldsymbol{\alpha}$. While the former case, corresponding to the reflecting lattice planes parallel to the platelet faces, utilizes the longitudinal piezoelectric effect and is more convenient experimentally, it will be shown that, with the exception of four crystal classes ($\bar{6},\bar{6}m2,23,\bar{4}3m$) the complete set of piezoelectric constants cannot be determined in this manner. On the other hand, the second configuration, which utilizes the transverse piezoelectric effect and corresponds to the electric field lying in the reflecting planes, requires larger experimental effort to eliminate distortion of the electric field near the side faces of the sample, but permits the determination of the complete set of piezoelectric constants for all twenty piezoelectric crystal classes.

In the following section explicit expressions of the right-hand side (r.h.s.) of equation (12) will be given for all twenty piezoelectric crystal classes and for both experimental configurations.

Application to piezoelectric crystal classes

Denoting for convenience the r.h.s. of equation (12) by L and T for parallel-field and perpendicular-field reflection, corresponding to the longitudinal and transverse piezoelectric effects, respectively, equation (12) may be rewritten as

$$-\cot\theta\left(\frac{\partial\theta}{\partial E}\right)=\begin{cases}L(\boldsymbol{\alpha}\|\mathbf{N})\\T(\boldsymbol{\alpha}\perp\mathbf{N})\end{cases}, \tag{13}$$

where

$$L=N_rN_iN_jd_{rij}\quad(\boldsymbol{\alpha}=\mathbf{N}) \tag{14a}$$

$$T=\alpha_rN_iN_jd_{rij}\quad(\boldsymbol{\alpha}\,.\,\mathbf{N}=0)\,. \tag{14b}$$

For the numerical application of these equations the form of the piezoelectric constant tensor corresponding to a particular crystal class must be used, and both the lattice plane normal $\mathbf{N}$ and the direction $\boldsymbol{\alpha}$ of the electric field must be expressed in terms of the Miller indices. For the components of the unit vector $\mathbf{N}$ the corresponding relation is obtained from equations (3) and (11) and is for the general triclinic case given by the familiar expression [*International Tables for X-ray Crystallography* (1959)] ($i=1,2,3$):

$$N_i=ha_i^*+kb_i^*+lc_i^*/[h^2a^{*2}+k^2b^{*2}+l^2c^{*2}+2klb^*c^*\cos\alpha^*+2hla^*c^*\cos\beta^*+2hka^*b^*\cos\gamma^*]^{1/2}. \tag{15}$$

Here a^*,b^*,c^* denote the lattice constants, and $\alpha^*,\beta^*,\gamma^*$ the angles between the unit-cell vectors $\mathbf{a}^*,\mathbf{b}^*,\mathbf{c}^*$ of the reciprocal lattice. a_i^*,b_i^*,c_i^* $(i=1,2,3)$ denote the Cartesian coordinates of $\mathbf{a}^*,\mathbf{b}^*,\mathbf{c}^*$, respectively, in the same coordinate system to which the piezoelectric constant tensor is referred.

For parallel-field reflection the unit vector $\boldsymbol{\alpha}$ is determined by the condition $\boldsymbol{\alpha}=\mathbf{N}$. For perpendicular-field reflection $\boldsymbol{\alpha}$ is constrained by the condition $\boldsymbol{\alpha}\,.\,\mathbf{N}=0$. Thus for a given lattice plane (hkl) the vector $\boldsymbol{\alpha}$ has one degree of freedom, which may be conveniently described by the angle φ according to

$$\boldsymbol{\alpha}=\cos\varphi\mathbf{U}+\sin\varphi\mathbf{V}\,, \tag{16}$$

where $\mathbf{U}$ is a unit vector perpendicular to $\mathbf{N}$ lying in the plane generated by the unit vector $\mathbf{e}_3$ in the x_3 direction, and by the lattice plane normal $\mathbf{N}$, and $\mathbf{V}$ is perpendicular to both $\mathbf{U}$ and $\mathbf{N}$. The vectors $\mathbf{U}$ and $\mathbf{V}$ are then given by

$$\mathbf{U}=[-(\mathbf{e}_3\,.\,\mathbf{N})\mathbf{N}+\mathbf{e}_3]/(N_1^2+N_2^2)^{1/2} \tag{17a}$$

$$\mathbf{V}=\mathbf{U}\times\mathbf{N}\,. \tag{17b}$$

Inserting (17*a*) and (17*b*) into (16), the components α_r of the unit vector $\boldsymbol{\alpha}$ may be expressed in terms of the components N_r of the lattice plane normal and of the angle φ according to

$$\alpha_1=-(N_1N_3\cos\varphi+N_2\sin\varphi)/(N_1^2+N_2^2)^{1/2} \tag{18a}$$

$$\alpha_2=-(N_2N_3\cos\varphi-N_1\sin\varphi)/(N_1^2+N_2^2)^{1/2} \tag{18b}$$

$$\alpha_3=(N_1^2+N_2^2)^{1/2}\cos\varphi\,. \tag{18c}$$

As will be discussed below, for most crystal classes convenient choices of the angle φ are possible if at least one of the Miller indices is zero. In these cases the vector $\boldsymbol{\alpha}$ lies along symmetry directions of the crystal, and a considerable simplification of the equations given below results.

By using the form of the piezoelectric tensor corresponding to the individual crystal classes as given, for example, by Nye (1957) the expressions L and T defined in (14*a*) and (14*b*) may be explicitly written out as given below for the twenty piezoelectric crystal classes. In the following, the piezoelectric constants will be expressed in Voigt notation, that is, the index pair ij in d_{rij} (with $r,i,j=1,2,3$) is replaced by a single index $\mu=1,2,3;4;5;6$ corresponding to $ij=11,22,33$; 23 and 32; 13 and 31; 12 and 21, respectively, and a factor of two is introduced for $\mu=4,5,6$, such that $d_{r\mu}=d_{rij}$ for $\mu=1,2,3$, and $d_{r\mu}=2d_{rij}$ for $\mu=4,5,6$. The following abbreviations are introduced in order to describe the coefficients of the piezoelectric constants occurring in the expression for T for the tetragonal, trigonal, hexagonal and cubic systems:

$$A_+=[-2N_1N_2N_3\cos\varphi+(N_1^2-N_2^2)\sin\varphi]N_3/(N_1^2+N_2^2)^{1/2} \tag{19a}$$

$$A_-=-N_3(N_1^2+N_2^2)^{1/2}\sin\varphi \tag{19b}$$

$$B_+=-N_3^2(N_1^2+N_2^2)^{1/2}\cos\varphi \tag{19c}$$

$$B_-=-[(N_1^2-N_2^2)N_3\cos\varphi+2N_1N_2\sin\varphi]N_3/(N_1^2+N_2^2)^{1/2} \tag{19d}$$

$$C_+=(N_1^2+N_2^2)^{3/2}\cos\varphi \tag{19e}$$

$$C_-=(N_1^2-N_2^2)\,(N_1^2+N_2^2)^{1/2}\cos\varphi \tag{19f}$$

$$D_1=-[(N_1^2-3N_2^2)N_1N_3\cos\varphi+(3N_1^2-N_2^2)N_2\sin\varphi]/(N_1^2+N_2^2)^{1/2} \tag{19g}$$

$$D_2=[(3N_1^2-N_2^2)N_2N_3\cos\varphi-(N_1^2-3N_2^2)N_1\sin\varphi]/(N_1^2+N_2^2)^{1/2} \tag{19h}$$

$$E=\{[3(N_1^2+N_2^2)-2]N_1N_2\cos\varphi+(N_1^2-N_2^2)N_3\sin\varphi\}/(N_1^2+N_2^2)^{1/2} \tag{19i}$$

$$F=N_3^2(N_1^2+N_2^2)^{1/2}\cos\varphi \tag{19j}$$

$$G=N_1N_2(N_1^2+N_2^2)^{1/2}\cos\varphi\,. \tag{19k}$$

The description of the direction $\boldsymbol{\alpha}$ of the electric field in terms of the angle φ as given in equation (18), and the use of the φ-dependent quantities defined in equations (19*a*) to (19*k*) are limited to the case $\mathbf{N}\neq\mathbf{e}_3$. For $\mathbf{N}=\mathbf{e}_3$ the angle φ is not defined. However, the special case $\mathbf{N}_3=\mathbf{e}_3$ is of interest only for the triclinic and monoclinic systems, and the quantity T defined in equation (14*b*) becomes in this case

$$T=\alpha_1d_{13}+\alpha_2d_{23}\,. \tag{20}$$

On the other hand, for the tetragonal, trigonal, hexagonal and cubic systems the quantity T is identically zero for $\mathbf{N}=\mathbf{e}_3$, so that this case need not be considered explicitly.

Triclinic system

Class $1(C_1)$. (Eighteen independent constants: d_{11}, d_{12}, d_{13}, d_{14}, d_{15}, d_{16}, d_{21}, d_{22}, d_{23}, d_{24}, d_{25}, d_{26}, d_{31}, d_{32}, d_{33}, d_{34}, d_{35}, d_{36}.)

$$\begin{aligned}L=\;&N_1^3d_{11}+N_1N_2^2(d_{12}+d_{26})+N_1N_3^2(d_{13}+d_{35})\\&+N_1^2N_2(d_{21}+d_{16})+N_2^3d_{22}+N_2N_3^2(d_{23}+d_{34})\\&+N_1^2N_3(d_{31}+d_{15})+N_2^2N_3(d_{32}+d_{24})+N_3^3d_{33}\\&+N_1N_2N_3(d_{14}+d_{25}+d_{36})\end{aligned} \tag{21a}$$

$$\begin{aligned}T=\;&\alpha_1N_1^2d_{11}+\alpha_1N_2^2d_{12}+\alpha_1N_3^2d_{13}\\&+\alpha_2N_1^2d_{21}+\alpha_2N_2^2d_{22}+\alpha_2N_3^2d_{23}\\&+\alpha_3N_1^2d_{31}+\alpha_3N_2^2d_{32}+\alpha_3N_3^2d_{33}\\&+\alpha_1N_2N_3d_{14}+\alpha_1N_1N_3d_{15}+\alpha_1N_1N_2d_{16}\\&+\alpha_2N_2N_3d_{24}+\alpha_2N_1N_3d_{25}+\alpha_2N_1N_2d_{26}\\&+\alpha_3N_2N_3d_{34}+\alpha_3N_1N_3d_{35}+\alpha_3N_1N_2d_{36}\,.\end{aligned} \tag{21b}$$

Monoclinic system

Class $2(C_2)$. (Eight independent constants: d_{14}, d_{16}, d_{21}, d_{22}, d_{23}, d_{25}, d_{34}, d_{36}.)

$$\begin{aligned} L= & N_2^3d_{22}+N_1^2N_2(d_{21}+d_{16})+N_2N_3^2(d_{23}+d_{34}) \\ & +N_1N_2N_3(d_{14}+d_{25}+d_{36}) \end{aligned} \tag{22a}$$

$$\begin{aligned} T= & \alpha_2N_1^2d_{21}+\alpha_2N_2^2d_{22}+\alpha_2N_3^2d_{23} \\ & +\alpha_1N_2N_3d_{14}+\alpha_1N_1N_2d_{16}+\alpha_2N_1N_3d_{25} \\ & +\alpha_3N_2N_3d_{34}+\alpha_3N_1N_2d_{36}\,. \end{aligned} \tag{22b}$$

Class $m(C_s)$. (Ten independent constants: d_{11}, d_{12}, d_{13}, d_{15}, d_{24}, d_{26}, d_{31}, d_{32}, d_{33}, d_{35}.)

$$\begin{aligned} L= & N_1^3d_{11}+N_1N_2^2(d_{12}+d_{26})+N_1N_3^2(d_{13}+d_{35}) \\ & +N_1^2N_3(d_{31}+d_{15})+N_2^2N_3(d_{32}+d_{24})+N_3^3d_{33} \end{aligned} \tag{23a}$$

$$\begin{aligned} T= & \alpha_1N_1^2d_{11}+\alpha_1N_2^2d_{12}+\alpha_1N_3^2d_{13} \\ & +\alpha_3N_1^2d_{31}+\alpha_3N_2^2d_{32}+\alpha_3N_3^2d_{33}+\alpha_1N_1N_3d_{15} \\ & +\alpha_2N_2N_3d_{24}+\alpha_2N_1N_2d_{26}+\alpha_3N_1N_3d_{35}\,. \end{aligned} \tag{23b}$$

Orthorhombic system

Class $222(D_2)$. (Three independent constants: d_{14}, d_{25}, d_{36}.)

$$L=N_1N_2N_3(d_{14}+d_{25}+d_{36}) \tag{24a}$$

$$T=\alpha_1N_2N_3d_{14}+\alpha_2N_1N_3d_{25}+\alpha_3N_1N_2d_{36}\,. \tag{24b}$$

Class $mm2(C_{2v})$. (Five independent constants: d_{15}, d_{24}, d_{31}, d_{32}, d_{33}.)

$$L=N_1^2N_3(d_{31}+d_{15})+N_2^2N_3(d_{32}+d_{24})+N_3^3d_{33} \tag{25a}$$

$$\begin{aligned} T= & \alpha_3N_1^2d_{31}+\alpha_3N_2^2d_{32}+\alpha_3N_3^2d_{33} \\ & +\alpha_1N_1N_3d_{15}+\alpha_2N_2N_3d_{24}\,. \end{aligned} \tag{25b}$$

Tetragonal system

Class $4(C_4)$. (Four independent constants: d_{14}, d_{15}, d_{31}, d_{33}.)

$$L=(N_1^2+N_2^2)N_3(d_{31}+d_{15})+N_3^3d_{33} \tag{26a}$$

$$T=C_+d_{31}+Fd_{33}+A_-d_{14}+B_+d_{15}\,. \tag{26b}$$

Class $\bar{4}(S_4)$. (Four independent constants: d_{14}, d_{15}, d_{31}, d_{36}.)

$$L=(N_1^2-N_2^2)N_3(d_{31}+d_{15})+N_1N_2N_3(2d_{14}+d_{36}) \tag{27a}$$

$$T=C_-d_{31}+A_+d_{14}+B_-d_{15}+Gd_{36}\,. \tag{27b}$$

Class $422(D_4)$. (One independent constant: d_{14}.)

$$L=0 \tag{28a}$$

$$T=A_-d_{14}\,. \tag{28b}$$

Class $4mm(C_{4v})$. (Three independent constants: d_{15}, d_{31}, d_{33}.)

$$L=(N_1^2+N_2^2)N_3(d_{31}+d_{15})+N_3^3d_{33} \tag{29a}$$

$$T=C_+d_{31}+Fd_{33}+B_+d_{15}\,. \tag{29b}$$

Class $\bar{4}2m(D_{2d})$. (Two independent constants: d_{14}, d_{36}.)

$$L=N_1N_2N_3(2d_{14}+d_{36}) \tag{30a}$$

$$T=A_+d_{14}+Gd_{36}\,. \tag{30b}$$

Trigonal system

Class $3(C_3)$. (Six independent constants: d_{11}, d_{14}, d_{15}, d_{22}, d_{31}, d_{33}.)

$$\begin{aligned} L= & (N_1^2-3N_2^2)N_1d_{11}-(3N_1^2-N_2^2)N_2d_{22}+N_3^3d_{33} \\ & +(N_1^2+N_2^2)N_3(d_{31}+d_{15}) \end{aligned} \tag{31a}$$

$$T=D_1d_{11}+D_2d_{22}+C_+d_{31}+FD_{33}+A_-d_{14}+B_+d_{15}\,. \tag{31b}$$

Class $32(D_3)$. (Two independent constants: d_{11}, d_{14}.)

$$L=(N_1^2-3N_2^2)N_1d_{11} \tag{32a}$$

$$T=D_1d_{11}+A_-d_{14}\,. \tag{32b}$$

Class $3m(C_{3v})$. (Four independent constants: d_{15}, d_{22}, d_{31}, d_{33}.)

$$\begin{aligned} L= & -(3N_1^2-N_2^2)N_2d_{22} \\ & +(N_1^2+N_2^2)N_3(d_{31}+d_{15})+N_3^3d_{33} \end{aligned} \tag{33a}$$

$$T=D_2d_{22}+C_+d_{31}+Fd_{33}+B_+d_{15}\,. \tag{33b}$$

Hexagonal system

Class $6(C_6)$. (Four independent constants: d_{14}, d_{15}, d_{31}, d_{33}.)

$$L=(N_1^2+N_2^2)N_3(d_{31}+d_{15})+N_3^3d_{33} \tag{34a}$$

$$T=C_+d_{31}+Fd_{33}+A_-d_{14}+B_+d_{15}\,. \tag{34b}$$

Class $\bar{6}(C_{3h})$. (Two independent constants: d_{11}, d_{22}.)

$$L=(N_1^2-3N_2^2)N_1d_{11}-(3N_1^2-N_2^2)N_2d_{22} \tag{35a}$$

$$T=D_1d_{11}+D_2d_{22}\,. \tag{35b}$$

Class $622(D_6)$. (One independent constant: d_{14}.)

$$L=0 \tag{36a}$$

$$T=A_-d_{14}\,. \tag{36b}$$

Class $6mm(C_{6v})$. (Three independent constants: d_{15}, d_{31}, d_{33}.)

$$L=(N_1^2+N_2^2)N_3(d_{31}+d_{15})+N_3^3d_{33} \tag{37a}$$

$$T=C_+d_{31}+Fd_{33}+B_+d_{15}\,. \tag{37b}$$

Class $\bar{6}m2(D_{3h})$. (One independent constant: d_{11}.)

$$L=(N_1^2-3N_2^2)N_1d_{11} \tag{38a}$$

$$T=D_1d_{11}\,. \tag{38b}$$

Classes $23(T)$ *and* $\bar{4}3m(T_d)$. (One independent constant: d_{14}.)

$$L=3N_1N_2N_3d_{14} \tag{39a}$$

$$T=Ed_{14}\,. \tag{39b}$$

As mentioned above, equations (26*b*), (27*b*), *etc.* to (39*b*) are valid only for $\mathbf{N} \neq \mathbf{e}_3$, and for $\mathbf{N} = \mathbf{e}_3$ the quantity T in these equations is identically zero.

Equations (21*a*) to (39*a*) represent the most general form of the expressions for the longitudinal piezoelectric effect for the 20 piezoelectric crystal classes. Each lattice plane (*hkl*) is characterized by its effective piezoelectric coefficient $L = L_{hkl}$, which for triclinic symmetry is obtained by inserting equation (15) into equation (21*a*), and for the crystal classes of higher symmetry by inserting the simplified form of equation (15) appropriate for the particular crystal symmetry into the corresponding equations (22*a*) to (39*a*). For each lattice plane (*hkl*) the electric field coefficient $-\cot\theta(\partial\theta/\partial E)$ of the Bragg angle $\theta = \theta_{hkl}$ gives according to (13) an experimental value for the corresponding linear combination L_{hkl} of piezoelectric constants. While no further simplification is possible for triclinic symmetry, it will be shown below that for the crystal classes of higher symmetry the expressions for L given by equations (22*a*) to (39*a*) may become much simpler if one or two of the Miller indices are zero. However, in several instances the coefficients of the piezoelectric constants in the expressions for L vanish, unless all three Miller indices are nonzero. Thus for the experimental determination of the complete set of piezoelectric constants the most general form of the expressions for L as given in equations (21*a*) to (39*a*) has to be used.

Similarly, equations (21*b*) to (39*b*) represent the most general form of the expressions for the transverse piezoelectric effect in terms of the components of the reflecting lattice plane normal **N**, the direction $\boldsymbol{\alpha}$ of the electric field, and the coefficients A_+, A_-, *etc.* defined in equations (19*a*) to (19*k*). According to equations (18*a*) to (18*c*) the components of $\boldsymbol{\alpha}$, and according to equations (19*a*) to (19*k*) the coefficients A_+, A_-, *etc.* depend on the components of **N** and on the free parameter φ defined in (16). The components of **N**, in turn, depend on the Miller indices according to (15). Thus all coefficients of the piezoelectric constants in the expressions for T depend on the Miller indices in a rather

Table 1. *Crystal plate normal* $\boldsymbol{\alpha} = (\alpha_1\alpha_2\alpha_3)$, *Miller indices* (*hkl*), *face normal of reflecting plane* $\mathbf{N} = (N_1N_2N_3)$, *and expressions for L and T defined in equations* (14*a*) *and* (14*b*) *for monoclinic system* ($a^* = 1/a \sin\beta$; $b^* = 1/b$; $c^* = 1/c \sin\beta$; $C = \cos\beta$; $S = \sin\beta$)

The base vectors **b** and **c** coincide with the Y and Z axes, respectively, and the base vector **a** lies in the X–Z plane, forming an angle $\beta > 90°$ with the **c** axis.

Class	$\vec{\alpha}$	$(hk\ell)$	$\vec{N}$	$\xi;\eta;\zeta;R$	L,T
$2(C_2)$ (8 constants)	(010)	(0k0)	(010)		$L=d_{22}$
		$(h0\ell)$	$(\xi 0 \zeta)$	$\xi=(ha^*-\ell c^*C)/R;\zeta=\ell c^*S/R$ $R=[h^2a^{*2}+\ell^2c^{*2}-2h\ell a^*c^*C]^{1/2}$	$T=\xi^2d_{21}+\zeta^2d_{23}+\xi\zeta d_{25}$
	(001)	(hk0)	$(\xi\eta 0)$	$\xi=ha^*/R;\eta=kb^*/R$ $R=[h^2a^{*2}+k^2b^{*2}]^{1/2}$	$T=\xi\eta d_{36}$
	$(\bar{\eta}\xi 0)$	(hk0)	$(\xi\eta 0)$	$\xi=ha^*/R;\eta=kb^*/R$ $R=[h^2a^{*2}+k^2b^{*2}]^{1/2}$	$T=\xi^3d_{21}+\xi\eta^2d_{22}-\xi\eta^2d_{16}$
	$(\xi\eta\zeta)$	$(hk\ell)$	$(\xi\eta\zeta)$	$\xi=(ha^*-\ell c^*C)/R;\eta=kb^*/R;\zeta=\ell c^*S/R$ $R=[h^2a^{*2}+k^2b^{*2}+\ell^2c^{*2}-2h\ell a^*c^*C]^{1/2}$	$L=\eta^3d_{22}+\xi^2\eta(d_{21}+d_{16})+\eta\zeta^2(d_{23}+d_{34})+\xi\eta\zeta(d_{14}+d_{25}+d_{36})$
$m(C_s)$ (10 constants)	(100)	(h00)	(100)		$L=d_{11}$
		(0k0)	(010)		$T=d_{12}$
	(001)	(hk0)	$(\xi\eta 0)$	$\xi=ha^*/R;\eta=kb^*/R$ $R=[h^2a^{*2}+k^2b^{*2}]^{1/2}$	$T=\xi^2d_{31}+\eta^2d_{32}$
	$(\bar{\eta}\xi 0)$	(hk0)	$(\xi\eta 0)$	$\xi=ha^*/R;\eta=kb^*/R$ $R=[h^2a^{*2}+k^2b^{*2}]^{1/2}$	$T=-\xi^2\eta d_{11}-\eta^3d_{12}+\xi^2\eta d_{26}$
	$(\bar{\zeta}0\xi)$	$(h0\ell)$	$(\xi 0 \zeta)$	$\xi=(ha^*-\ell c^*C)/R;\zeta=\ell c^*S/R$ $R=[h^2a^{*2}+\ell^2c^{*2}-2h\ell a^*c^*C]^{1/2}$	$T=-\xi^2\zeta d_{11}-\zeta^3d_{13}+\xi^3d_{31}+\xi\zeta^2d_{33}-\xi\zeta^2d_{15}+\xi^2\zeta d_{35}$
	$(\xi 0 \zeta)$	$(h0\ell)$	$(\xi 0 \zeta)$	$\xi=(ha^*-\ell c^*C)/R;\zeta=\ell c^*S/R$ $\zeta=[h^2a^{*2}+\ell^2c^{*2}-2h\ell a^*c^*C]^{1/2}$	$L=\xi^3d_{11}+\xi\zeta^2(d_{13}+d_{35})+\xi^2\zeta(d_{31}+d_{15})+\zeta^3d_{33}$
	$(\xi\eta\zeta)$	$(hk\ell)$	$(\xi\eta\zeta)$	$\xi=(ha^*-\ell c^*C)/R;\eta=kb^*/R;\zeta=\ell c^*S/R$ $R=[h^2a^{*2}+k^2b^{*2}+\ell^2c^{*2}-2h\ell a^*c^*C]^{1/2}$	$L=\xi^3d_{11}+\xi\eta^2(d_{12}+d_{26})+\xi\zeta^2(d_{13}+d_{35})+\xi^2\zeta(d_{31}+d_{15})+$ $+\eta^2\zeta(d_{32}+d_{24})+\zeta^3d_{33}$

involved manner. While for triclinic symmetry the equations have to be used in this form, a considerable simplification occurs if one or two of the Miller indices are zero. However, for the two monoclinic crystal classes 2 and *m* the coefficients of some piezoelectric constants (those of d_{14} and d_{34} for class 2, and of d_{24} for class *m*) vanish in these special cases. Therefore the complete set of piezoelectric constants cannot be determined solely from measurements of the transverse piezoelectric effect perpendicular to these special lattice planes. In these cases one has to use the general form of equations (22*b*) and (23*b*) for the transverse piezoelectric effect or, alternatively, supplement the equations for the transverse piezoelectric effect for the special set of lattice planes with one Miller index zero by the general equations (22*a*) and (23*a*) for the longitudinal piezoelectric effect.

In Tables 1 to 5 the simplified relations obtained from equations (22*a*) and (22*b*) to (38*a*) and (38*b*) are presented that result for the longitudinal and transverse piezoelectric coefficients *L* and *T* in the monoclinic, orthorhombic, tetragonal, trigonal and hexagonal classes if at least one of the Miller indices is zero. For the monoclinic and orthorhombic classes the general expressions for the longitudinal piezoelectric coefficients *L* have also been included because they are needed for the experimental determination of the complete set of piezoelectric constants. For completeness, the equation for *L* for the two isometric classes 23 and $\bar{4}3m$ is also presented as Table 6. The explanation of Tables 1 to 6 is given below.

The simpler equations presented in Tables 1 to 6 are sufficient for the experimental determination of the complete set of piezoelectric constants for all crystal classes, except for triclinic symmetry. Therefore the general form of the equations (22*a*) and (22*b*) to (39*a*) and (39*b*) need not be considered in the design of actual experiments. It may happen in certain cases, however, that for the lattice planes with at least one Miller index zero that are listed in Tables 1 to 6 the structure factor may be inconveniently small, or vanish exactly. In these cases and for triclinic symmetry one has to resort to the general equations (21) to (39).

It is apparent from equations (21*a*), (22*a*), *etc.* to (39*a*), that some of the piezoelectric constants enter the expressions for *L* only in the form of linear combinations, so that the complete set of piezoelectric constants cannot be determined from parallel-field reflection measurements ($\boldsymbol{\alpha}=\mathbf{N}$) alone. Exceptions are the four classes $\bar{6}$, $\bar{6}m2$, 23 and $\bar{4}3m$, for which the quantity *L* depends on the individual piezoelectric constants only, so that they can be determined from parallel-field reflection alone. For all other classes, perpendicular-field reflection measurements ($\boldsymbol{\alpha}\,.\,\mathbf{N}=0$) are required in addition to, or instead of, parallel-field reflection measurements.

Table 2. *Crystal plate normal* $\boldsymbol{\alpha}=(\alpha_1\alpha_2\alpha_3)$, *Miller indices* (*hkl*), *face normal of reflecting plane* $\mathbf{N}=(N_1N_2N_3)$ *and expressions of L and T defined in equations* (14*a*) *and* (14*b*) *for orthorhombic system*

Class	$\vec{\alpha}$	(hkℓ)	$\vec{N}$	ξ;η;ζ;R	L,T
222(D_2)	(100)	(0kℓ)	(0ηζ)	$\eta=k/bR;\zeta=\ell/cR$ $R=[k/b)^2+(\ell/c)^2]^{1/2}$	$T=\eta\zeta d_{14}$
(3 constants)	(010)	(h0ℓ)	(ξ0ζ)	$\xi=h/aR;\zeta=\ell/cR$ $R=[(h/a)^2+(\ell/c)^2]^{1/2}$	$T=\xi\zeta d_{25}$
	(001)	(hk0)	(ξη0)	$\xi=h/aR;\eta=k/bR$ $R=[(h/a)^2+(\ell/c)^2]^{1/2}$	$T=\xi\eta d_{36}$
	(ξηζ)	(hkℓ)	(ξηζ)	$\xi=h/aR;\eta=k/bR;\zeta=\ell/cR$ $R=[(h/a)^2+(k/b)^2+(\ell/c)^2]^{1/2}$	$L=\xi\eta\zeta(d_{14}+d_{25}+d_{36})$
mm2(C_{2v})	(001)	(hk0)	(ξη0)	$\xi=h/aR;\eta=k/bR$ $R=[(h/a)^2+(k/b)^2]^{1/2}$	$T=\xi^2d_{31}+\eta^2d_{32}$
		(00ℓ)	(001)		$L=d_{33}$
(5 constants)	($\bar{\zeta}$0ξ)	(h0ℓ)	(ξ0ζ)	$\xi=h/aR;\zeta=\ell/cR$ $R=[(h/a)^2+(\ell/c)^2]^{1/2}$	$T=\xi^3d_{31}+\xi\zeta^2d_{33}-\xi\zeta^2d_{15}$
	(0$\bar{\zeta}$η)	(0kℓ)	(0ηζ)	$\eta=k/bR;\zeta=\ell/cR$ $R=[(k/b)^2+(\ell/c)^2]^{1/2}$	$T=\eta^3d_{32}+\eta\zeta^2d_{33}-\eta\zeta^2d_{24}$
	(ξηζ).	(hkℓ)	(ξηζ)	$\xi=h/aR;\eta=k/bR;\zeta=\ell/cR$ $R=[(h/a)^2+(k/b)^2+(\ell/c)^2]^{1/2}$	$L=\xi^2\zeta(d_{31}+d_{15})+\eta^2\zeta(d_{32}+d_{24})+\zeta^3d_{33}$

Another noteworthy feature of the above equations is that for the six classes 4, 422, 3, 32, 6, 622, the piezoelectric constant d_{14} does not enter the equations for L and therefore cannot be determined at all from parallel-field reflection measurements.

According to equations (21*b*), (22*b*), *etc.* to (39*b*) the quantity T depends in all cases on all individual piezoelectric constants. Exceptions are particular directions of $\mathbf{N}$ and/or values of φ, for which some of the coefficients given in equations (19*a*) to (19*k*) may become equal, or vanish. In general, however, it is possible to determine the complete set of piezoelectric constants from a sufficiently large number of perpendicular-field reflection measurements alone. In practice, however, it is desirable to use as many parallel-field reflection measurements as possible, because the specimen preparation is simpler and experimental errors may be expected to be smaller in this case.

Specimen orientation

For the measurement of the longitudinal piezoelectric effect crystal platelets with electroded pairs of (*hkl*) faces with normal $\mathbf{N}=\boldsymbol{\alpha}$ are required. For the transverse piezoelectric effect platelets with electroded pairs of faces with normal $\boldsymbol{\alpha}$ perpendicular to the normal $\mathbf{N}$ of the reflecting (*hkl*) face must be prepared. In both cases it is desirable to choose the direction $\mathbf{N}$, and in the second case also the direction $\boldsymbol{\alpha}$, along high-symmetry directions (parallel to rotation axes, perpendicular to or within mirror planes) so as to achieve accurate orientation and reduce the effort required for the orientation and preparation of the platelets. However, since either or both piezoelectric effects may vanish along some symmetry directions the requirement of non-vanishing piezoelectric effect eliminates many otherwise suitable lattice planes. It is further desirable

Table 3. *Crystal plate normal* $\boldsymbol{\alpha}=(\alpha_1\alpha_2\alpha_3)$, *Miller indices* (*hkl*), *face normal of reflecting plane* $\mathbf{N}=(N_1N_2N_3)$, *and expressions for L and T defined in equations* (14*a*) *and* (14*b*) *for tetragonal system*

Class	$\vec{\alpha}$	$(hk\ell)$	$\vec{N}$	$\xi;\eta;\zeta;R$	L,T
$4(C_4)$ (4 constants)	(100)	$(0k\ell)$	$(0\eta\zeta)$	$\eta=k/aR;\zeta=\ell/cR$ $R=[(k/a)^2+(\ell/c)^2]^{1/2}$	$T=\eta\zeta d_{14}$
	(001)	(00ℓ)	(001)		$L=d_{33}$
		$(hk0)$	$(\xi\eta0)$	$\xi=h/R;\eta=k/R$ $R=[h^2+k^2]^{1/2}$	$T=d_{31}$
	$(\bar{\zeta}0\xi)$	$(h0\ell)$	$(\xi0\zeta)$	$\xi=h/aR,\zeta=\ell/cR$ $R=[(h/a)^2+(\ell/c)^2]^{1/2}$	$T=\xi^3d_{31}+\xi\zeta^2d_{33}-\xi\zeta^2d_{15}$
$\bar{4}(S_4)$ (4 constants)	(100)	$(0k\ell)$	$(0\eta\zeta)$	$\eta=k/aR;\zeta=\ell/cR$ $R=[(k/a)^2+(\ell/c)^2]^{1/2}$	$T=\eta\zeta d_{14}$
	(001)	$(hk0)$	$(\xi\eta0)$	$\xi=h/R;\eta=k/R$ $R=[h^2+k^2]^{1/2}$	$T=(\xi^2-\eta^2)d_{31}+\xi\eta d_{36}$
	$(\bar{\zeta}0\xi)$	$(h0\ell)$	$(\xi0\zeta)$	$\xi=h/aR;\zeta=\ell/cR$ $R=[(h/a)^2+(\ell/c)^2]^{1/2}$	$T=\xi^3d_{31}-\xi\zeta^2d_{15}$
$422(D_4)$ (1 constant)	(100)	$(0k\ell)$	$(0\eta\zeta)$	$\eta=k/aR;\zeta=\ell/cR$ $R=[(k/a)^2+(\ell/c)^2]^{1/2}$	$T=\eta\zeta d_{14}$
$4mm(C_{4v})$ (3 constants)	(001)	(00ℓ)	(001)		$L=d_{33}$
		$(hk0)$	$(\xi\eta0)$	$\xi=h/R;\eta=k/R$ $R=[h^2+k^2]^{1/2}$	$T=d_{31}$
	$(\bar{\zeta}0\xi)$	$(h0\ell)$	$(\xi0\zeta)$	$\xi=h/aR;\zeta=\ell/cR$ $R=[(h/a)^2+(\ell/c)^2]^{1/2}$	$T=\xi^3d_{31}+\xi\zeta^2d_{33}-\xi\zeta^2d_{15}$
$\bar{4}2m(D_{2d})$ (2 constants)	(100)	$(0k\ell)$	$(0\eta\zeta)$	$\eta=k/aR;\zeta=\ell/cR$ $R=[(k/a)^2+(\ell/c)^2]^{1/2}$	$T=\eta\zeta d_{14}$
	(001)	$(hk0)$	$(\xi\eta0)$	$\xi=h/R;\eta=k/R$ $R=[h^2+k^2]^{1/2}$	$T=\xi\eta d_{36}$

that for a given platelet normal **α** several non-equivalent side faces (hkl) exist, which lead to different linear combinations of piezoelectric constants in the expression for the transverse piezoelectric coefficient T. Ideally, it would be desirable to determine the complete set of piezoelectric constants from one polygon-shaped crystal platelet with several side faces, so as to require only one pair of electroded surfaces for measuring the longitudinal piezoelectric effect in the direction of the plate normal **α**, and the transverse effect for several non-equivalent side face normals **N**. Unfortunately, this ideal design is possible only for some of the high-symmetry crystal classes. In general, more than one type of crystal platelet is required for determining the complete set of piezoelectric constants. In this case it is desirable to perform the measurements mostly, or if possible, exclusively, on the basis of the longitudinal effect, because the corresponding platelets require only one pair of parallel faces and are therefore easier to prepare than platelets for the measurement of the transverse effect, and because measurements of the longitudinal effect can be done more accurately and more easily than those of the transverse effect. As mentioned above, this can only be achieved for the four classes $\bar{6}$, $\bar{6}m2$, 23 and $\bar{4}3m$.

For the triclinic system no symmetry directions exist, so that (at least) 18 platelets corresponding to 18 different face normals **α** are required. Since according to equation (21*a*) the longitudinal piezoelectric coefficient L depends on 10 linear combinations of piezoelectric constants, 10 of the 18 platelets may be chosen such that their faces correspond to 10 different (hkl) planes. The remaining (minimum of) eight platelets must be prepared for the transverse piezoelectric effect in such a manner that the normals **α** of the pair of large electroded surfaces are perpendicular to eight different

Table 4. *Crystal plate normal* $\mathbf{\alpha}=(\alpha_1\alpha_2\alpha_3)$, *Miller–Bravais indices* (hkl), *for hexagonal indexing, face normal of reflecting plane* $\mathbf{N}=(N_1N_2N_3)$, *and expressions L and T defined in equations* (14*a*) *and* (14*b*) *for trigonal system*

Class	$\vec{\alpha}$	$(hk\ell)$	$\vec{N}$	$\xi;\eta;\zeta;R$	L,T
	(100)	$(2h,\bar{h},0)$	(100)		$L=d_{11}$
$3(C_3)$		$(0k\ell)$	$(0\eta\zeta)$	$\eta=2k/\sqrt{3}aR;\zeta=\ell/cR$	$T=-\eta^2d_{11}+\eta\zeta d_{14}$
				$R=[(4/3)(k/a)^2+(\ell/c)^2]^{1/2}$	
(6 constants)	(010)	(0k0)	(010)		$L=d_{22}$
		$(2h,\bar{h},\ell)$	$(\xi0\zeta)$	$\xi=2h/aR;\zeta=\ell/cR$	$T=-\xi^2d_{22}-\xi\zeta d_{14}$
				$R=[(2h/a)^2+(\ell/c)^2]^{1/2}$	
	(001)	(00ℓ)	(001)		$L=d_{33}$
		$(2h,k-h,0)$	$(\xi\eta0)$	$\xi=\sqrt{3}h/R;\eta=k/R$	$T=d_{31}$
				$R=[3h^2+k^2]^{1/2}$	
	$(0\eta\zeta)$	$(0k\ell)$	$(0\eta\zeta)$	$\eta=2k/\sqrt{3}aR;\zeta=\ell/cR$	$L=\eta^3d_{22}+\zeta^3d_{33}+\eta^2\zeta(d_{31}+d_{15})$
				$R=[(4/3)(k/a)^2+(\ell/c)^2]^{1/2}$	
	$(0\bar{\zeta}\eta)$	$(0k\ell)$	$(0\eta\zeta)$	$\eta=2k/\sqrt{3}aR;\zeta=\ell/cR$	$T=-\eta^2\zeta d_{22}+\eta\zeta^2d_{33}+\eta^3d_{31}-\eta\zeta^2d_{15}$
				$R=[(4/3)(k/a)^2+(\ell/c)^2]^{1/2}$	
	(100)	$(2h,\bar{h},0)$	(100)		$L=d_{11}$
$32(D_3)$		$(0k\ell)$	$(0\eta\zeta)$	$\eta=2k/\sqrt{3}aR;\zeta=\ell/cR$	$T=-\eta^2d_{11}+\eta\zeta d_{14}$
(2 constants)				$R=[(4/3)(k/a)^2+\ell/c)^2]^{1/2}$	
	(010)	(0k0)	(010)		$L=d_{22}$
$3m(C_{3v})$	(001)	(00ℓ)	(001)		$L=d_{33}$
		$(2h,k-h,0)$	$(\xi\eta0)$	$\xi=\sqrt{3}h/R;\eta=k/R$	$T=d_{31}$
(4 constants)				$R=[3h^2+k^2]^{1/2}$	
	$(0\eta\zeta)$	$(0k\ell)$	$(0\eta\zeta)$	$\eta=2k/\sqrt{3}aR;\zeta=\ell/cR$	$L=\eta^3d_{22}+\zeta^3d_{33}+\eta^2\zeta(d_{31}+d_{15})$
				$R=[(4/3)(k/a)^2+(\ell/c)^2]^{1/2}$	
	$(0\bar{\zeta}\eta)$	$(0k\ell)$	$(0\eta\zeta)$	$\eta=2k/\sqrt{3}aR;\zeta=\ell/cR$	$T=-\eta^2\zeta d_{22}+\eta\zeta^2d_{33}+\eta^3d_{31}-\eta\zeta^2d_{15}$
				$R=[(4/3)(k/a)^2+(\ell/c)^2]^{1/2}$	

(hkl) side faces. The resulting piezoelectric coefficients depend on the orientation of the crystallographic axes with respect to the Cartesian coordinate system chosen. It is recommended to use the base vectors of the direct and reciprocal lattice according to the 1949 I.R.E. convention (*Standards on Piezoelectric Crystals*, 1949):

$$\begin{aligned}
\mathbf{a} &= (a\sin\beta,\ 0,\ a\cos\beta)\\
\mathbf{b} &= (-b\sin\alpha\cos\gamma^*,\ b\sin\alpha\sin\gamma^*,\ b\cos\alpha)\\
\mathbf{c} &= (0,\ 0,\ c)\\
\mathbf{a}^* &= (a^*\sin\gamma^*,\ a^*\cos\gamma^*,\ 0)\\
\mathbf{b}^* &= (0,\ b^*,\ 0)\\
\mathbf{c}^* &= (-c^*\sin\alpha^*\cos\beta,\ c^*\cos\alpha^*,\ c^*\sin\alpha^*\sin\beta)\ .
\end{aligned}$$

Here (*International Tables for X-ray Crystallography*, 1959):

$$a^* = \frac{bc\sin\alpha}{V}\ ,\ etc.$$

$$V = 2abc\sin\frac{\alpha+\beta+\gamma}{2}\sin\frac{-\alpha+\beta+\gamma}{2}$$

$$\times\sin\frac{\alpha-\beta+\gamma}{2}\sin\frac{\alpha+\beta-\gamma}{2}$$

$$\cos\alpha^* = (\cos\beta\cos\gamma-\cos\alpha)/\sin\beta\sin\gamma,\ etc.$$

and further $\alpha > 90°$, $\beta > 90°$.

For the symmetry classes of higher symmetry the 1949 I.R.E. convention (*Standards on Piezoelectric

Table 6. *Crystal plate normal, Miller indices* (hkl), *face normal of reflecting plane* $\mathbf{N} = (N_1N_2N_3)$, *and expression L defined in equation* (14*a*) *for isometric classes* 23 *and* $\bar{4}3m$

$\boldsymbol{\alpha}$	(hkl)	$\mathbf{N}$	$\xi;\ \eta;\ \zeta;\ R$	L
($\xi\eta\zeta$)	(hkl)	($\xi\eta\zeta$)	$\xi=h/R;\ \eta=k/R;\ \zeta=l/R$ $R=[h^2+k^2+l^2]^{1/2}$	$3\xi\eta\zeta d_{14}$

Table 5. *Crystal plate normal* $\boldsymbol{\alpha} = (\alpha_1\alpha_2\alpha_3)$, *Miller–Bravais indices* (hkl), *face normal of reflecting plane* $\mathbf{N} = (N_1N_2N_3)$, *and expressions L and T defined in equations* (14*a*) *and* (14*b*) *for hexagonal system*

Class	$\vec{\alpha}$	($hk\ell$)	$\vec{N}$	$\xi;\eta;\zeta;R$	L,T
$6(C_6)$ (4 constants)	(100)	($0k\ell$)	($0\eta\zeta$)	$\eta=2k/\sqrt{3}aR;\zeta=\ell/cR$ $R=[(4/3)(k/a)^2+(\ell/c)^2]^{1/2}$	$T=\eta\zeta d_{14}$
	(001)	(00ℓ)	(001)		$L=d_{33}$
		($2h,k-h,0$)	($\xi\eta 0$)	$\xi=\sqrt{3}h/R;\eta=k/R$ $R=[3h^2+k^2]^{1/2}$	$T=d_{31}$
	($0\eta\zeta$)	($0k\ell$)	($0\eta\zeta$)	$\eta=2k/\sqrt{3}aR;\zeta=\ell/cR$ $R=[(4/3)(k/a)^2+(\ell/c)^2]^{1/2}$	$L=\zeta^3d_{33}+\eta^2\zeta(d_{31}+d_{15})$
	($0\bar{\zeta}\eta$)	($0k\ell$)	($0\eta\zeta$)	$\eta=2k/\sqrt{3}aR;\zeta=\ell/cR$ $R=[(4/3)(k/a)^2+(\ell/c)^2]^{1/2}$	$T=\eta\zeta^2d_{33}+\eta^3d_{31}-\eta\zeta^2d_{15}$
$\bar{6}(C_{3h})$ (2 constants)	(100)	($2h,\bar{h},0$)	(100)		$L=d_{11}$
	(010)	($0k0$)	(010)		$L=d_{22}$
$622(D_6)$ (1 constant)	(100)	($0k\ell$)	($0\eta\zeta$)	$\eta=2k/\sqrt{3}aR;\zeta=\ell/cR$ $R=[(4/3)(k/a)^2+(\ell/c)^2]^{1/2}$	$T=\eta\zeta d_{14}$
$6mm(C_{6v})$ (3 constants)	(001)	(00ℓ)	(001)		$L=d_{33}$
		($2h,k-h,0$)	($\xi\eta 0$)	$\xi=\sqrt{3}h/R;\eta=k/R$ $R=[3h^2+k^2]^{1/2}$	$T=d_{31}$
	($0\eta\zeta$)	($0k\ell$)	($0\eta\zeta$)	$\eta=2k/\sqrt{3}aR;\zeta=\ell/cR$ $R=[(4/3)(k/a)^2+(\ell/c)^2]^{1/2}$	$L=\zeta^3d_{33}+\eta^2\zeta(d_{31}+d_{15})$
	($0\bar{\zeta}\eta$)	($0k\ell$)	($0\eta\zeta$)	$\eta=2k/\sqrt{3}aR;\zeta=\ell/cR$ $R=[(4/3)(k/a)^2+(\ell/c)^2]^{1/2}$	$T=\eta\zeta^2d_{33}+\eta^3d_{31}-\eta\zeta^2d_{15}$
$\bar{6}m2(D_{3h})$ (1 constant)	(100)	($2h,\bar{h},0$)	(100)		$L=d_{11}$

Crystals, 1949) is easily summarized as follows. The twofold axes of class $2(C_2)$ and the mirror plane normal of class $m(C_s)$ coincide with the crystallographic **b** axis, which is placed along the positive Y direction of a right-handed Cartesian coordinate system. The **c** axis is placed along the positive Z direction, and the **a** axis (being normal to the **b** axis and forming an angle $\beta > 90°$ with the **c** axis) is lying in the XZ plane. For the orthorhombic, tetragonal and cubic systems the crystallographic axes coincide with the X, Y and Z axes. For the trigonal and hexagonal systems the threefold (or sixfold) axis is parallel to the Z axis, and the positive X axis coincides with any of the three secondary axes $\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3$ perpendicular to the threefold (or sixfold) axes. The Y axis is perpendicular to the X and Z axes, so as to form a right-handed Cartesian coordinate system.

Discussion of Tables 1 to 6

For the remaining 19 piezoelectric crystal classes the existence of symmetry elements reduces not only the number of independent piezoelectric constants, but also leads to the existence of high-symmetry directions $\boldsymbol{\alpha}$ with non-vanishing longitudinal and/or transverse piezoelectric effect. In Tables 1 to 6 such pairs of high-symmetry directions $\boldsymbol{\alpha}, \mathbf{N}$, the associated Miller indices *hkl* and the quantities L or T describing the longitudinal and transverse piezoelectric effect as defined in equations (14*a*) and (14*b*) are listed for the crystal classes of the monoclinic, orthorhombic, tetragonal, trigonal, hexagonal and cubic systems, respectively. In the crystal classes of lower symmetry the number of high-symmetry directions is too small for determining the complete set of the piezoelectric constants. In these cases the expressions for both $\boldsymbol{\alpha}$ and $\mathbf{N}$ and for the associated values of L and/or T are also given for a general set of Miller indices.

The results in Table 1 indicate that for the class $C_2(2)$ the eight independent constants may be determined from five crystal platelets. From one platelet with orientation $\boldsymbol{\alpha} = (010)$ it is possible to determine the four constants d_{21}, d_{22}, d_{23} and d_{25}, but for the remaining four constants d_{14}, d_{16}, d_{34} and d_{36} one crystal plate each is required. If the platelet with orientation $\boldsymbol{\alpha} = (010)$ has three side faces corresponding to three sets of non-equivalent Miller indices $h0l$, measurement of the longitudinal effect gives d_{22}, and of the transverse effect perpendicular to each of the three side faces gives three linear combinations each of the constants d_{21}, d_{23} and d_{25}. Of the remaining four measurements three may be made by using the longitudinal effect and give (if the above mentioned constants d_{21}, d_{22}, d_{23} and d_{25} have been determined independently) the constants d_{16}, d_{34}, $d_{14} + d_{36}$. In order to determine the constants d_{14} and d_{36} individually, one additional measurement based on the transverse effect is required.

For the determination of the 10 independent constants of class $C_s(m)$ nine platelets with different orientations are required. While the platelet with $\boldsymbol{\alpha} = (100)$ permits to determine d_{11} through the longitudinal effect, and d_{12} through the transverse effect, the remaining eight constants require for their determination one platelet each. While five linear combinations of these constants (d_{26}, $d_{13} + d_{35}$, $d_{31} + d_{15}$, $d_{32} + d_{34}$, d_{33}) may be determined from the longitudinal effect, the remaining three independent measurements must be based on the transverse effect.

As shown by the data in Table 2 the three independent piezoelectric constants of class 222 have to be determined from the transverse effect by using three different crystal platelets with faces normal to the three coordinate axes, respectively. The longitudinal effect on a platelet with a pair of general (*hkl*) faces permits an independent measurement of the sum $d_{14} + d_{25} + d_{36}$.

The determination of the five independent constants for class $mm2(C_{2v})$ is illustrated below with the aid of a numerical example.

The discussion of Tables 3 to 6 for the remaining crystal classes proceeds along the same lines as above and need not be explicitly presented here.

Numerical example

In order to illustrate and facilitate the use of Tables 1 to 6 the expressions for L and T required for the determination of the five independent constants of Bi_3TiNbO_9 (crystal class *mm*2) will be given here. The crystal structure of Bi_3TiNbO_9 has been refined from X-ray and neutron diffraction data by Wolfe, Newnham, Smith & Kay (1971). These authors list the observed and calculated absolute values of the structure factors of a large number of non-equivalent reflections, from which suitable high-intensity reflections can be selected.

According to Table 2 the three constants d_{31}, d_{32} and d_{33} can be determined from one platelet with a pair of electroded (001) faces, if the longitudinal effect is measured by Bragg reflection on the (001) face, resulting in d_{33}, and if the transverse effect is measured by Bragg reflection on two different side faces of the type (*hk*0), which gives two different linear combinations of d_{31} and d_{32}. Based on the structure factors listed by Wolfe, Newnham, Smith & Kay (1971) we select the three reflections 0,0,10, 040, and 400. The corresponding face normals $\mathbf{N}$ are (0,0,1), (0,1,0) and (1,0,0), respectively. From the lattice constants $a = 5{\cdot}431$, $b = 5{\cdot}389$ and $c = 25{\cdot}050$ Å given by Wolfe, Newnham, Smith & Kay (1971) the corresponding Bragg angles are calculated for Cu $K\alpha$ radiation and are listed in Table 7, together with the values of *hkl*, with the structure factors, and with the values of the platelet normal $\boldsymbol{\alpha}$ and the values $\mathbf{N}$ of the three reflecting lattice planes. In Fig. 1(*a*) the shape and orientation of the platelet with faces corresponding to these three normals and the corresponding Bragg angles θ_1, θ_2 and θ_3 are illustrated schematically. Also listed in Table 7 are the corresponding values of L and T obtained from the last column of Table 2. According to equation (13) these quantities are equal to the electric field coefficient $-\cot\theta_i(\partial\theta_i/\partial E)$ ($i=1,2,3$) of the associated Bragg angle. Denoting the experimental values of the electric field coefficient by M_i ($i=1,2,3$) the three piezoelectric constants d_{33}, d_{32} and d_{31} are then given by the first three equalities listed in the last column of Table 7. According to Table 2 the remaining two constants d_{15} and d_{24} have to be determined from the transverse piezoelectric effect on two different platelets with side faces ($h0l$) and ($0kl$), with the corresponding normals of the side faces ($\xi0\zeta$) and ($0\eta\zeta$), respectively, and with normals ($\bar{\zeta}0\xi$) and ($0\bar{\zeta}\eta$) of the electroded main faces In the fifth column of Table 2 the components ($\xi\eta\zeta$) of these two normals are expressed in terms of the *hkl* values. On the basis of the structure factors listed by Wolfe, Newnham, Smith & Kay (1971) we select the reflections 0,2,10 and 2,0,10. In Table 7 their structure factors, the normals **N** of the side faces and the normals **α** of the electroded main faces as calculated from columns 2, 4 and 5 of Table 2 are listed together with the associated Bragg angles θ_4 and θ_5. The orientation of these two platelets and the location of the two Bragg

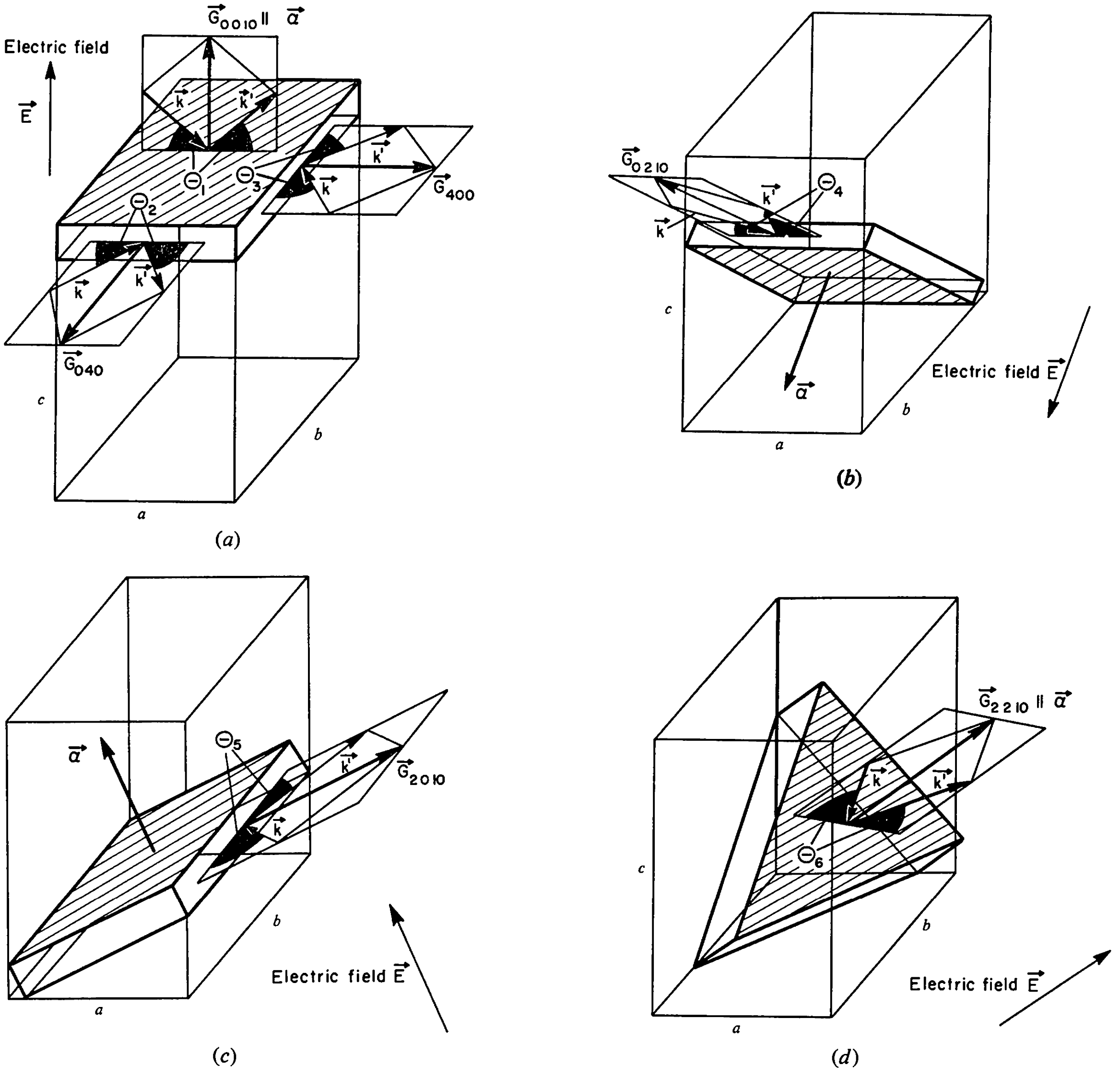

Fig. 1. Orientation of four crystal platelets showing electroded faces as hatched areas and indicating location of six reflecting (*hkl*) faces with their associated reciprocal lattice vectors $\mathbf{G}_{hkl}$, wave vectors **K** and **K′** of incident and scattered beam, respectively, and Bragg angles $\theta_1,\theta_2,\ldots,\theta_6$, required for measurement of six independent electric field coefficients $-\cot\theta_i$ $(\partial\theta_i/\partial E)$ as chosen in Table 7 for determining the five piezoelectric constants of Bi_3TiNbO_9 (class *mm*2). (Figures are schematic and not to scale.) (*a*) (001) platelet for determining electric field coefficient of θ_1 through longitudinal piezoelectric effect, and of θ_2 and θ_3 through transverse piezoelectric effect; (*b*) platelet for determining electric field coefficient of θ_4 through transverse piezoelectric effect; (*c*) platelet for determining electric field coefficient of θ_5 through transverse piezoelectric effect; (*d*) (115) platelet for determining electric field coefficient of θ_6 through longitudinal piezoelectric effect.

Table 7. *Miller indices hkl, calculated structure factors* $|F_c|$ [*in units given by Wolfe, Newnham, Smith & Kay* (1971)], *face normals* **N** *of crystal platelets representing reflecting lattice planes, face normals* $\boldsymbol{\alpha}$ *of electroded crystal platelet surfaces, representing direction of electric field* **E**, *label i denoting six different experimental configurations, Bragg angle* θ_i *for* Cu $K\alpha$, *type of piezoelectric effect* (L = *longitudinal*, T = *transverse*), *and l.h.s. and r.h.s. of equation* (12), *consisting of electric field coefficients* $M_i = -\cot\,\theta_i(\partial\theta_i/\partial E)$ (*to be determined experimentally*) *and of linear combination* $\alpha_r N_i N_j d_{rij}$ *of piezoelectric constants for* Bi_3TiNbO_9, *as obtained from entries of Table 2 for crystal class* $mm2(C_{2v})$

hkl	$\lvert F_c\rvert$	$\mathbf{N}=(N_1,N_2,N_3)$	$\boldsymbol{\alpha}=(\alpha_1,\alpha_2,\alpha_3)$	*i*	θ_i	Type	$-\cot\,\theta_i(\partial\theta_i/\partial E)=\alpha_r N_iN_jd_{rij}$
0 0 10	836	(0, 0, 1)	(0, 0, 1)	1	17·909°	L	$M_1=d_{33}$
0 4 0	683	(0, 1, 0)	(0, 0, 1)	2	34·873	T	$M_2=d_{32}$
4 0 0	668	(1, 0, 0)	(0, 0, 1)	3	34·565	T	$M_3=d_{31}$
0 2 10	785	(0, 0·6809, 0·7324)	(0, −0·7324, 0·6809)	4	24·826	T	$M_4=0{\cdot}3157d_{32}$ $+0{\cdot}3652(d_{33}-d_{24})$
2 0 10	796	(0·6780, 0, 0·7350)	(−0·7350, 0, 0·6780)	5	24·731	T	$M_5=0{\cdot}3117d_{31}$ $+0{\cdot}3663(d_{33}-d_{15})$
2 2 10	633	(0·5598, 0·5642, 0·6069)	(0·5598, 0·5642, 0·6069)	6	30·445	L	$M_6=0{\cdot}1902(d_{31}+d_{15})$ $+0{\cdot}1932(d_{32}+d_{24})+0{\cdot}2235d_{33}$

angles θ_4 and θ_5 is illustrated in Fig. 1(*b*) and (*c*). The last column of Table 7 gives the corresponding expressions for the quantity T obtained from the last column of Table 2. If experimental values of the electrical field coefficient $M_i = -\cot\,\theta_i(\partial\theta_i/\partial E)$ are available for all five Bragg angles θ_i ($i=1,2,\ldots,5$) described, the equations given in the last column of Table 7 for $M_1, M_2, \ldots, M_5$ represent five equations for the five unknown piezoelectric constants d_{33}, d_{32}, d_{31}, d_{24} and d_{15}.

According to Table 2 an additional independent measurement of the longitudinal effect on a general (*hkl*) plane gives a linear combination of all five piezoelectric constants. Choosing for this purpose the 2,2,10 reflection gives the entries listed on the last line of Table 7. The platelet orientation and the Bragg angle θ_6 are illustrated in Fig. 1(*d*). The six expressions for $M_1, M_2, \ldots, M_6$ listed in Table 7 represent six equations for the five unknown piezoelectric constants. Their best values can be obtained from a standard simultaneous least-squares fit.

For better accuracy additional platelets representing different values of (0*kl*), (*h*0*l*) or (*hkl*) may be used *ad lib*. It should be noted that for a given (*hkl*) face higher-order and lower-order reflections corresponding to different Bragg angles may be measured and should give the same value for the electric field coefficient. For example, the longitudinal field coefficient of all (00*l*) reflections should be equal to d_{33} for any value of *l*. While the lower-order reflections 002, 004, 006, 008 are of lower intensity than the 0,0,10 reflection, the reflection 0,0,20 is also relatively strong and may be used to obtain an additional independent value for d_{33}.

In order to reduce the experimental errors arising from the specimen orientation it appears more appropriate, however, to use additional crystal platelets representing different values of (0*kl*), (*h*0*l*), or (*hkl*), which would lead to different numerical coefficients of the piezoelectric constants in the equations for M_4, M_5 and M_6, respectively.

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