Condensed Matter Physics, 2003, Vol. 6, No. 2(34), pp. 333–345

Non-linear mechanical, electrical and thermal phenomena in piezoelectric crystals

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Received August 25, 2002, in final form March 31, 2003

Mechanical, electrical and thermal phenomena occurring in piezoelectric crystals were examined by non-linear approximation. For this purpose, use was made of the thermodynamic function of state, which describes an anisotropic body. Considered was the Gibbs function. The calculations included strain tensor $\varepsilon_{ij} = f(\sigma_{kl}, E_n, T)$, induction vector $D_m = f(\sigma_{kl}, E_n, T)$ and entropy $S = f(\sigma_{kl}, E_n, T)$ as function of stress σ_{kl}, field strength E_n and temperature difference T. The equations obtained apply to anisotropic piezoelectric bodies provided that the "forces" σ_{kl}, E_n, T acting on the crystal are known.

Key words: *piezoelectric crystals, thermodynamics, anisotropic bodies, tensors*

PACS: *65.40.-b, 77.65.-j, 77.65.Bn, 77.65.Ly, 05.70.Ce*

1. Introduction

The present paper provides a thermodynamic description of elastic (mechanical), electrical and thermal properties of crystals in a non-linear approximation. The physical processes and phenomena that occur in a real crystal generally are of a non-linear character, similarly to those in any other physical body which displays a certain degree of nonlinearity. It is conventional to describe non-linear properties (i.e., physical nonlinearity) in terms of higher-order material constants, and such are the factors of proportionality incorporated in the Taylor series expansion of a non-linear relation describing the given effect. In general, the mentioned constants are tensors.

Nonlinearity manifests in the values of the second-order material constants being the functions of the values of the applied forces which act onto the crystal, e.g. the elasticity constants can be a function of the applied stress σ. Thus, the standard Hooke equation may be written as follows:

$$\varepsilon = s(\sigma)\sigma, \tag{1.1}$$

where ε denotes strain and $s(\sigma)$ is an elasticity constant which varies according to the stress σ applied. Hence, $s(\sigma)$ takes the form

$$s(\sigma) = s_1 + s_2\sigma + s_3\sigma^2 + \ldots , \tag{1.2}$$

where s_1 is a second-order material constant (modulus of elasticity).

By linear approximation, equation (1.1) becomes as follows: $\varepsilon = s_1\sigma$, where $s_1 = \partial\varepsilon/\partial\sigma$.

Using non-linear approximation, we have

$$\varepsilon = \frac{\partial\varepsilon}{\partial\sigma}\sigma + \frac{1}{2!}\frac{\partial^2\varepsilon}{\partial\sigma^2}\sigma^2 + \frac{1}{3!}\frac{\partial^3\varepsilon}{\partial\sigma^3}\sigma^3 + \ldots ,$$

where

$$s_1 = \frac{\partial\varepsilon}{\partial\sigma}, \qquad s_2 = \frac{1}{2!}\frac{\partial^2\varepsilon}{\partial\sigma^2}, \qquad s_3 = \frac{1}{3!}\frac{\partial^3\varepsilon}{\partial\sigma^3}.$$

The coefficients $s_1, s_2, s_3, \ldots$ of equation (1.2) can be regarded as material constants which are proportional to the stresses (σ) of relevant powers. Hence, they are material constants of second, third, fourth or higher order. Thus, the Hooke equation for non-linear effects can be written as [1,2]

$$\varepsilon = s(\sigma)\sigma = s_1\sigma + s_2\sigma^2 + s_3\sigma^3 + \ldots \qquad \text{or} \qquad \varepsilon = (s_1 + s_2\sigma + s_3\sigma^2 + \ldots)\sigma.$$

With tensor notation for anisotropic bodies, the relation of

$$s = s_1 + s_2\sigma + s_3\sigma^2 + \ldots$$

takes the following form:

$$s = s_{ijkl} + s_{ijklpq}\sigma_{pq} + s_{ijklpqrs}\sigma_{pq}\sigma_{rs} + \ldots$$

and the Hooke equation

$$\varepsilon = s(\sigma)\sigma = s_1\sigma + s_2\sigma^2 + s_3\sigma^3 + \ldots$$

becomes

$$\varepsilon_{ij} = s_{ijkl}\sigma_{kl} + s_{ijklpq}\sigma_{pq}\sigma_{kl} + s_{ijklpqrs}\sigma_{pq}\sigma_{rs}\sigma_{kl} + \ldots$$

in tensor notation, where s_{ijkl} is a fourth-order tensor (second-order material constant), s_{ijklpq} is a sixth-order tensor (third-order material constant), $s_{ijklpqrs}$ is an eight-order tensor (fourth-order material constant), and the coefficients i, j, k, l, p, q, r, s take the values of 1, 2, 3. Summation signs have been omitted [1,3,4].

Higher-order material constants are formally derived from thermodynamic functions. The procedure is similar to that for the linear case. If, for example, strain ε is produced simultaneously by stress σ, by electric field E, and temperature variations T, the equation of state for non-linear processes, which includes material constants only up to the third order, can be written as

$$\varepsilon = s_1\sigma + d_1E + \alpha_1T + s_2\sigma^2 + d_2E^2 + \alpha_2T^2 + k_{\sigma E}\sigma E + k_{\sigma T}\sigma T + k_{ET}ET,$$

where

$$s_1 = \frac{\partial\varepsilon}{\partial\sigma}, \quad d_1 = \frac{\partial\varepsilon}{\partial E}, \quad \alpha_1 = \frac{\partial\varepsilon}{\partial T}, \quad s_2 = \frac{1}{2}\frac{\partial^2\varepsilon}{\partial\sigma^2}, \quad d_2 = \frac{1}{2}\frac{\partial^2\varepsilon}{\partial E^2},$$
$$\alpha^2 = \frac{1}{2}\frac{\partial^2\varepsilon}{\partial T^2}, \quad k_{\sigma E} = \frac{\partial^2\varepsilon}{\partial\sigma\partial E}, \quad k_{\sigma T} = \frac{\partial^2\varepsilon}{\partial\sigma\partial T}, \quad k_{ET} = \frac{\partial^2\varepsilon}{\partial E\partial T}.$$

Apart from second-order material constants, s_1, d_1, α_1, and third-order material constants s_2, d_2, α_2, there are also third-order "mixed" material constants $k_{\sigma E}, k_{\sigma T}$ and k_{ET}. The order of the material constant is defined by the order of the derivative of the thermodynamic function and not by the order of the "force" acting onto the crystal or by the order of the material constant tensor.

The problem will be presented more in detail in section 2.

2. Thermodynamic relations in crystals and Gibbs functions

According to the first law of thermodynamics, the total energy U of a body is the sum of different energy types. In piezoelectric crystals, energy balance is primarily accounted for by mechanical, electrical and thermal energy. The effect of magnetic energy or gravitational energy on the phenomena occurring in piezoelectric crystals may be neglected. In general, there are eight thermodynamic functions that can be used to describe a piezoelectric phenomenon. The form of the function depends on the choice of the independent variables, selected according to the conditions under which the crystal is to be examined [2].

In the present paper we confine ourselves to thermodynamics, that is, Gibbs function G. Mathematical analysis enables us to define particular material constants, as well as to establish many interesting relations between them, by linear and non-linear approximation.

$$G = U - \varepsilon_{ij}\sigma_{ij} - E_m D_m - TS, \tag{2.1}$$

where $i, j, m = 1, 2, 3$.

Let us consider the differential form $\mathrm{d}G$, which describes the state of the crystal following the application of three different "forces" – stress σ_{ij}, electric field E_m, and temperature T. The forces acting onto the crystal are independent variables. Thus, we have

$$\mathrm{d}G = \mathrm{d}U - \varepsilon_{ij}\mathrm{d}\sigma_{ij} - \sigma_{ij}\mathrm{d}\varepsilon_{ij} - E_m\mathrm{d}D_m - D_m\mathrm{d}E_m - S\mathrm{d}T - T\mathrm{d}S. \tag{2.2}$$

By virtue of the first and second law of thermodynamics,

$$\mathrm{d}U = \sigma_{ij}\mathrm{d}\varepsilon_{ij} + E_m\mathrm{d}D_m + T\mathrm{d}S, \tag{2.3}$$

where $i, j, m = 1, 2, 3$.

Substituting (2.3) into (2.2), we obtain

$$\mathrm{d}G = -\varepsilon_{ij}\mathrm{d}\sigma_{ij} - D_m\mathrm{d}E_m - S\mathrm{d}T. \tag{2.4}$$

Strain ε_{ij}, induction D_m and entropy S are functions of stress σ_{kl}, electric field E_n and temperature T:

$$\varepsilon_{ij} = f(\sigma_{kl}, E_n, T), \quad D_m = f(\sigma_{kl}, E_n, T), \quad S = f(\sigma_{kl}, E_n, T).$$

Differentiating the function G with respect to individual independent variables, and having determined the remaining values, we obtain

$$\mathrm{d}G = \left(\frac{\partial G}{\partial \sigma_{ij}}\right)_{E,T} \mathrm{d}\sigma_{ij} + \left(\frac{\partial G}{\partial E_m}\right)_{\sigma,T} \mathrm{d}E_m + \left(\frac{\partial G}{\partial T}\right)_{\sigma,E} \mathrm{d}T. \tag{2.5}$$

Comparing the coefficients of (2.4) and (2.5), we can derive the relations that describe particular quantities:

$$\varepsilon_{ij} = -\left.\frac{\partial G}{\partial \sigma_{ij}}\right|_{E,T}, \quad D_m = -\left.\frac{\partial G}{\partial E_m}\right|_{\sigma,T}, \quad S = -\left.\frac{\partial G}{\partial T}\right|_{\sigma,E}.$$

The indices in the lower part of the vertical line show the independent variable, which takes a constant value during differentiation.

The function ε_{ij}, D_m and S can be expanded into a Taylor series. All derivatives incorporated in the Taylor's series are the material constants.

2.1. Material constants derived from function ε_{ij}

Second-order elasticity constant

$$\left.\frac{\partial \varepsilon_{ij}}{\partial \sigma_{kl}}\right|_{E,T} = \frac{\partial}{\partial \sigma_{kl}}\left(-\frac{\partial G}{\partial \sigma_{ij}}\right) = -\left.\frac{\partial^2 G}{\partial \sigma_{kl}\partial \sigma_{ij}}\right|_{E,T} = s_{ijkl}^{E,T}\,.$$

Second-order piezoelectric constant

$$\left.\frac{\partial \varepsilon_{ij}}{\partial E_n}\right|_{\sigma,T} = \frac{\partial}{\partial E_n}\left(-\frac{\partial G}{\partial \sigma_{ij}}\right) = -\left.\frac{\partial^2 G}{\partial E_n\partial \sigma_{ij}}\right|_{T} = d_{ijn}^{T}\,.$$

Second-order piezocalorific constant

$$\left.\frac{\partial \varepsilon_{ij}}{\partial T}\right|_{\sigma,E} = \frac{\partial}{\partial T}\left(-\frac{\partial G}{\partial \sigma_{ij}}\right) = -\left.\frac{\partial^2 G}{\partial T\partial \sigma_{ij}}\right|_{E} = \alpha_{ij}^{E}\,.$$

Third-order elasticity constant

$$\left.\frac{\partial^2 \varepsilon_{ij}}{\partial \sigma_{kl}\partial \sigma_{pq}}\right|_{E,T} = \frac{\partial^2}{\partial \sigma_{kl}\partial \sigma_{pq}}\left(-\frac{\partial G}{\partial \sigma_{ij}}\right) = -\left.\frac{\partial^3 G}{\partial \sigma_{kl}\partial \sigma_{pq}\partial \sigma_{ij}}\right|_{E,T} = s_{ijklpq}^{E,T}\,.$$

Third-order piezoelectric constant

$$\left.\frac{\partial^2 \varepsilon_{ij}}{\partial \sigma_{kl}\partial E_n}\right|_{T} = \frac{\partial^2}{\partial \sigma_{kl}\partial E_n}\left(-\frac{\partial G}{\partial \sigma_{ij}}\right) = -\left.\frac{\partial^3 G}{\partial \sigma_{kl}\partial E_n\partial \sigma_{ij}}\right|_{T} = d_{ijkln}^{T}\,.$$

Third-order piezocalorific constant

$$\left.\frac{\partial^2 \varepsilon_{ij}}{\partial \sigma_{kl} \partial T}\right|_E = \frac{\partial^2}{\partial \sigma_{kl} \partial T}\left(-\frac{\partial G}{\partial \sigma_{ij}}\right) = -\left.\frac{\partial^3 G}{\partial \sigma_{kl} \partial T \partial \sigma_{ij}}\right|_E = \alpha^E_{ijkl}\,.$$

Third-order electrostriction constant

$$\left.\frac{\partial^2 \varepsilon_{ij}}{\partial E_n \partial E_t}\right|_{\sigma,T} = \frac{\partial^2}{\partial E_n \partial E_t}\left(-\frac{\partial G}{\partial \sigma_{ij}}\right) = -\left.\frac{\partial^3 G}{\partial E_n \partial E_t \partial \sigma_{ij}}\right|_T = o^T_{ijnt}\,.$$

Third-order constant

$$\left.\frac{\partial^2 \varepsilon_{ij}}{\partial E_n \partial T}\right|_{\sigma} = \frac{\partial^2}{\partial E_n \partial T}\left(-\frac{\partial G}{\partial \sigma_{ij}}\right) = -\frac{\partial^3}{\partial E_n \partial T \partial \sigma_{ij}} = k_{ijn}\,.$$

Third-order thermal expansion constant

$$\left.\frac{\partial^2 \varepsilon_{ij}}{\partial T \partial T_1}\right|_{\sigma,E} = \frac{\partial^2}{\partial T \partial T_1}\left(-\frac{\partial G}{\partial \sigma_{ij}}\right) = -\left.\frac{\partial^3 G}{\partial T \partial T_1 \partial \sigma_{ij}}\right|_E = r^E_{ij}\,.$$

2.2. Material constants derived from function D_m

Second-order piezoelectric constant

$$\left.\frac{\partial D_m}{\partial \sigma_{kl}}\right|_{E,T} = \frac{\partial}{\partial \sigma_{kl}}\left(-\frac{\partial G}{\partial E_m}\right) = -\left.\frac{\partial^2 G}{\partial \sigma_{kl} \partial E_m}\right|_T = d^T_{klm}\,.$$

Second-order permittivity constant

$$\left.\frac{\partial D_m}{\partial E_n}\right|_{\sigma,T} = \frac{\partial}{\partial E_n}\left(-\frac{\partial G}{\partial E_m}\right) = -\left.\frac{\partial^2 G}{\partial E_n \partial E_m}\right|_{\sigma,T} = \varepsilon^{\sigma,T}_{mn}\,.$$

Second-order electric heat constant

$$\left.\frac{\partial D_m}{\partial T}\right|_{\sigma,E} = \frac{\partial}{\partial T}\left(-\frac{\partial G}{\partial E_m}\right) = -\left.\frac{\partial^2 G}{\partial T \partial E_m}\right|_{\sigma} = p^{\sigma}_m\,.$$

Third-order piezoelectric constant

$$\left.\frac{\partial^2 D_m}{\partial \sigma_{kl} \partial \sigma_{pq}}\right|_{E,T} = \frac{\partial^2}{\partial \sigma_{kl} \partial \sigma_{pq}}\left(-\frac{\partial G}{\partial E_m}\right) = -\left.\frac{\partial^3 G}{\partial \sigma_{kl} \partial \sigma_{pq} \partial E_m}\right|_T = d^T_{klpqm}\,.$$

Third-order electrostriction constant

$$\left.\frac{\partial^2 D_m}{\partial \sigma_{kl} \partial E_n}\right|_T = \frac{\partial^2}{\partial \sigma_{kl} \partial E_n}\left(-\frac{\partial G}{\partial E_m}\right) = -\left.\frac{\partial^3 G}{\partial \sigma_{kl} \partial E_n \partial E_m}\right|_T = o^T_{klmn}\,.$$

Third-order constant

$$\left.\frac{\partial^2 D_m}{\partial \sigma_{kl} \partial T}\right|_E = \frac{\partial^2}{\partial \sigma_{kl} \partial T}\left(-\frac{\partial G}{\partial E_m}\right) = -\frac{\partial^3}{\partial \sigma_{kl} \partial T \partial E_m} = k_{klm}\,.$$

Third-order permittivity constant

$$\left.\frac{\partial^2 D_m}{\partial E_n \partial E_t}\right|_{\sigma,T} = \frac{\partial^2}{\partial E_n \partial E_t}\left(-\frac{\partial G}{\partial E_m}\right) = -\left.\frac{\partial^3 G}{\partial E_n \partial E_t \partial E_m}\right|_{\sigma,T} = \varepsilon^{\sigma,T}_{mnt} \, .$$

Third-order electric heat constant

$$\left.\frac{\partial^2 D_m}{\partial E_n \partial T}\right|_{\sigma} = \frac{\partial^2}{\partial E_n \partial T}\left(-\frac{\partial G}{\partial E_m}\right) = -\left.\frac{\partial^3 G}{\partial E_n \partial T \partial E_m}\right|_{\sigma} = p^{\sigma}_{mn} \, .$$

Third-order pyroelectric constant

$$\left.\frac{\partial^2 D_m}{\partial T_1 \partial T}\right|_{\sigma,E} = \frac{\partial^2}{\partial T_1 \partial T}\left(-\frac{\partial G}{\partial E_m}\right) = -\left.\frac{\partial^3 G}{\partial T_1 \partial T \partial E_m}\right|_{\sigma} = u^{\sigma}_{m} \, .$$

2.3. Material constants derived from function S

Second-order piezocalorific constant

$$\left.\frac{\partial S}{\partial \sigma_{kl}}\right|_{E,T} = \frac{\partial}{\partial \sigma_{kl}}\left(-\frac{\partial G}{\partial T}\right) = -\left.\frac{\partial^2 G}{\partial \sigma_{kl} \partial T}\right|_{E} = \alpha^{E}_{kl} \, .$$

Second-order electric heat constant

$$\left.\frac{\partial S}{\partial E_n}\right|_{\sigma,T} = \frac{\partial}{\partial E_n}\left(-\frac{\partial G}{\partial T}\right) = -\left.\frac{\partial^2 G}{\partial E_n \partial T}\right|_{\sigma} = p^{\sigma}_{n} \, .$$

Second-order thermal capacity constant

$$\left.\frac{\partial S}{\partial T}\right|_{\sigma,E} = \frac{\partial}{\partial T}\left(-\frac{\partial G}{\partial T_1}\right) = -\left.\frac{\partial^2 G}{\partial T \partial T_1}\right|_{\sigma,E} = \xi^{\sigma,E} \, .$$

Third-order piezocalorific constant

$$\left.\frac{\partial^2 S}{\partial \sigma_{kl} \partial \sigma_{pq}}\right|_{E,T} = \frac{\partial^2}{\partial \sigma_{kl} \partial \sigma_{pq}}\left(-\frac{\partial G}{\partial T}\right) = -\left.\frac{\partial^3 G}{\partial \sigma_{kl} \partial \sigma_{pq} \partial T}\right|_{E} = \alpha^{E}_{klpq} \, .$$

Third-order constant

$$\left.\frac{\partial^2 S}{\partial \sigma_{kl} \partial E_n}\right|_{T} = \frac{\partial^2}{\partial \sigma_{kl} \partial E_n}\left(-\frac{\partial G}{\partial T}\right) = -\frac{\partial^3}{\partial \sigma_{kl} \partial E_n \partial T} = k_{kln} \, .$$

Third-order thermal expansion constant

$$\left.\frac{\partial^2 S}{\partial \sigma_{kl} \partial T}\right|_{E} = \frac{\partial^2}{\partial \sigma_{kl} \partial T}\left(-\frac{\partial G}{\partial T_1}\right) = -\left.\frac{\partial^3 G}{\partial \sigma_{kl} \partial T \partial T_1}\right|_{E} = r^{E}_{kl} \, .$$

Third-order electric heat constant

$$\left.\frac{\partial^2 S}{\partial E_n \partial E_t}\right|_{\sigma,T} = \frac{\partial^2}{\partial E_n \partial E_t}\left(-\frac{\partial G}{\partial T}\right) = -\left.\frac{\partial^3 G}{\partial E_n \partial E_t \partial T}\right|_{\sigma} = p^{\sigma}_{nt} \, .$$

Third-order pyroelectric constant

$$\left.\frac{\partial^2 S}{\partial E_n \partial T}\right|_\sigma = \frac{\partial^2}{\partial E_n \partial T}\left(-\frac{\partial G}{\partial T_1}\right) = -\left.\frac{\partial^3 G}{\partial E_n \partial T \partial T_1}\right|_\sigma = u_n^\sigma \,.$$

Third-order thermal capacity constant

$$\left.\frac{\partial^2 S}{\partial T \partial T_1}\right|_{\sigma,E} = \frac{\partial^2}{\partial T \partial T_1}\left(-\frac{\partial G}{\partial T_2}\right) = -\left.\frac{\partial^3 G}{\partial T \partial T_1 \partial T_2}\right|_{\sigma,E} = \rho^{\sigma,E} \,.$$

2.4. Equalities between material constants

$$\begin{aligned}
&\left.\frac{\partial D_m}{\partial \sigma_{kl}}\right|_{E,T} = \left.\frac{\partial \varepsilon_{kl}}{\partial E_m}\right|_{\sigma,T} = d^T_{klm}\,, \qquad \left.\frac{\partial^2 S}{\partial \sigma_{kl}\partial \sigma_{pq}}\right|_{E,T} = \left.\frac{\partial^2 \varepsilon_{kl}}{\partial \sigma_{pq}\partial T}\right|_{E} = \alpha^E_{klpq}\,,\\
&\left.\frac{\partial D_m}{\partial \sigma_{kl}\partial \sigma_{pq}}\right|_{E,T} = \left.\frac{\partial^2 \varepsilon_{kl}}{\partial \sigma_{pq}\partial E_m}\right|_{T} = d^T_{klmpq}\,, \qquad \left.\frac{\partial^2 S}{\partial E_n \partial T}\right|_{\sigma} = \left.\frac{\partial D_n}{\partial T \partial T_1}\right|_{\sigma,E} = u^\sigma_n\,,\\
&\left.\frac{\partial S}{\partial E_n}\right|_{\sigma,T} = \left.\frac{\partial D_n}{\partial T}\right|_{\sigma,E} = p^\sigma_n\,, \qquad \left.\frac{\partial^2 S}{\partial \sigma_{kl}\partial T}\right|_{E} = \left.\frac{\partial^2 \varepsilon_{kl}}{\partial T \partial T_1}\right|_{\sigma,E} = r^E_{kl}\,,\\
&\left.\frac{\partial^2 S}{\partial E_n \partial E_t}\right|_{\sigma,T} = \left.\frac{\partial D_n}{\partial E_t \partial T}\right|_{\sigma} = p^\sigma_{nt}\,, \qquad \left.\frac{\partial D_m}{\partial \sigma_{kl}\partial E_n}\right|_{T} = \left.\frac{\partial^2 \varepsilon_{kl}}{\partial E_n \partial E_m}\right|_{\sigma,T} = o^T_{klmn}\,,\\
&\left.\frac{\partial S}{\partial \sigma_{kl}}\right|_{E,T} = \left.\frac{\partial \varepsilon_{kl}}{\partial T}\right|_{\sigma,E} = \alpha^E_{kl}\,, \qquad \left.\frac{\partial^2 \varepsilon_{ij}}{\partial E_n \partial T}\right|_{E} = \left.\frac{\partial^2 D_n}{\partial \sigma_{ij}\partial T}\right|_{E} = \left.\frac{\partial^2 S}{\partial \sigma_{ij}\partial E_n}\right|_{T} = k_{ijn}\,.
\end{aligned}$$

With the material constants (tensors) defined above, we can rewrite function ε_{ij}, D_m and S from Taylor series into form:

$$\begin{aligned}
\varepsilon_{ij} &= (s^{E,T}_{ijkl} + \tfrac{1}{2}s^{E,T}_{ijklpq}\sigma_{pq} + \tfrac{1}{2}d^T_{ijkln}E_n + \tfrac{1}{2}\alpha^E_{ijkl}T)\sigma_{kl}\\
&\quad + (d^T_{ijn} + \tfrac{1}{2}d^T_{klijn}\sigma_{kl} + \tfrac{1}{2}o^T_{ijnt}E_t + \tfrac{1}{2}k_{ijn}T)E_n\\
&\quad + (\alpha^E_{ij} + \tfrac{1}{2}\alpha^E_{ijkl}\sigma_{kl} + \tfrac{1}{2}k_{ijn}E_n + \tfrac{1}{2}r^E_{ij}T_1)T, \qquad (2.6)
\end{aligned}$$

$$\begin{aligned}
D_m &= (d^T_{mkl} + \tfrac{1}{2}d^T_{mklpq}\sigma_{pq} + \tfrac{1}{2}k_{mkl}T + \tfrac{1}{2}o^T_{klmn}E_n)\sigma_{kl}\\
&\quad + (\varepsilon^{T,\sigma}_{nm} + \tfrac{1}{2}\varepsilon^{T,\sigma}_{nmt}E_t + \tfrac{1}{2}o^T_{nmkl}\sigma_{kl} + \tfrac{1}{2}p^\sigma_{nm}T)E_n\\
&\quad + (p^\sigma_m + \tfrac{1}{2}k_{mkl}\sigma_{kl} + \tfrac{1}{2}p^\sigma_{mn}E_n + \tfrac{1}{2}u^\sigma_m T_1)T, \qquad (2.7)
\end{aligned}$$

$$\begin{aligned}
S &= (\alpha^E_{kl} + \tfrac{1}{2}\alpha^E_{klpq}\sigma_{pq} + \tfrac{1}{2}k_{kln}E_n + \tfrac{1}{2}r^E_{kl}T)\sigma_{kl}\\
&\quad + (p^\sigma_n + \tfrac{1}{2}k_{nkl}\sigma_{kl} + \tfrac{1}{2}p^\sigma_{nt}E_t + \tfrac{1}{2}u^\sigma_n T)E_n\\
&\quad + (\xi^{E,\sigma} + \tfrac{1}{2}r^E_{kl}\sigma_{kl} + \tfrac{1}{2}u^\sigma_n E_n + \rho^{E,\sigma}T_1)T. \qquad (2.8)
\end{aligned}$$

3. Linear and non-linear effects of the equations of state

Considering, for example, the equation of state derived from the Gibbs function G for non-linear effects, we can easily obtain the equations of state for linear effects by neglecting higher-order tensors. Thus, by virtue of (2.6), (2.7) and (2.8) we have

$$\begin{aligned} \varepsilon_{ij} &= s^{E,T}_{ijkl}\sigma_{kl} + d^{T}_{ijn}E_n + \alpha^{E}_{ij}T, \\ D_m &= d^{T}_{mkl}\sigma_{kl} + \varepsilon^{T,\sigma}_{nm}E_n + p^{\sigma}_{m}T, \\ S &= \alpha^{E}_{kl}\sigma_{kl} + p^{\sigma}_{n}E_n + \xi^{E,\sigma}T \end{aligned} \tag{3.1}$$

which are valid for linear effects [7,8,9].

By virtue of the symmetry of some tensors (tensor components in matrix tables), the relations of (3.1) can be presented in matrix form.

Hooke's law is often expressed in its contracted notation. Then, the equivalence between the components of the compliance fourth-rank tensor s_{ijkl} and the components of the 6×6 matrix s is shown to be:

$$\begin{aligned} s_{ijkl} &= s_{mn}\,, & m,n &= 1,2,3, \\ 2s_{ijkl} &= s_{mn}\,, & m &= 1,2,3,\ n = 4,5,6, \\ 4s_{ijkl} &= s_{mn}\,, & m,n &= 4,5,6 \end{aligned}$$

in which the following contraction rule is applied for replacing a pair of indices by a single contracted index: 11 $\to$ 1, 22 $\to$ 2, 33 $\to$ 3, (23, 32) $\to$ 4, (13, 31) $\to$ 5, (12, 21) $\to$ 6.

Furthermore, the full tensor suffixes of the stresses σ and strains ε are contracted according to the scheme:

$$\begin{aligned} &\sigma_{11} = \sigma_1\,, \qquad \sigma_{22} = \sigma_2\,, \qquad \sigma_{33} = \sigma_3\,, \\ &(\sigma_{23}, \sigma_{32}) = \sigma_4\,, \qquad (\sigma_{13}, \sigma_{31}) = \sigma_5\,, \qquad (\sigma_{12}, \sigma_{21}) = \sigma_6\,, \end{aligned}$$

$$\begin{aligned} &\varepsilon_{11} = \varepsilon_1\,, \qquad \varepsilon_{22} = \varepsilon_2\,, \qquad \varepsilon_{33} = \varepsilon_3\,, \\ &(2\varepsilon_{23}, 2\varepsilon_{32}) = \varepsilon_4\,, \qquad (2\varepsilon_{13}, 2\varepsilon_{31}) = \varepsilon_5\,, \qquad (2\varepsilon_{12}, 2\varepsilon_{21}) = \varepsilon_6 \end{aligned}$$

and

$$\begin{aligned} d_{ijk} &= d_{mn}\,, & m,n &= 1,2,3, \\ 2d_{ijk} &= d_{mn}\,, & m &= 1,2,3,\ n = 4,5,6, \end{aligned}$$

$$\begin{aligned} &\alpha_{11} = \alpha_1\,, \qquad \alpha_{22} = \alpha_2\,, \qquad \alpha_{33} = \alpha_3\,, \\ &(\alpha_{23}, \alpha_{32}) = \alpha_4, \qquad (\alpha_{13}, \alpha_{31}) = \alpha_5, \qquad (\alpha_{12}, \alpha_{21}) = \alpha_6\,. \end{aligned}$$

The relations of (3.1) constitute the starting set of the equations of state, which describe the environment, and they are widely used to solve the problems dealt with in piezoelectricity. Basic effects are described by the material constants (tensors) $s^{E,T}_{ijkl}$, $\varepsilon^{T,\sigma}_{nm}$, $\xi^{E,\sigma}$ that occur at the diagonal of the set of equations, whereas conjugate effects are defined by the remaining constants. On rewriting the material constants of (3.1) in a matrix form, we obtain a symmetrical matrix of linear effects:

$$\begin{bmatrix} \varepsilon_{ij} \\ D_m \\ S \end{bmatrix} = \begin{bmatrix} s^{E,T}_{ijkl} & d^T_{ijn} & \alpha^E_{ij} \\ d^T_{mkl} & \varepsilon^{T,\sigma}_{nm} & p^\sigma_m \\ \alpha^E_{kl} & p^\sigma_n & \xi^{E,\sigma} \end{bmatrix} \begin{bmatrix} \sigma_{kl} \\ E_n \\ T \end{bmatrix}. \tag{3.2}$$

The equivalence between the components of the compliance sixth-rank tensor s_{ijklpq} and the components of the 6×21 matrix is shown to be:

$$\begin{array}{rcll} S_{ijklpq} & = & s_{mno}\,, & m=1,2,3,\ n=o=1,2,3, \\ 2s_{ijklpq} & = & s_{mno}\,, & m=1,2,3,\ n\neq o,\ n=1,2,\ o=2,3, \\ 4s_{ijklpq} & = & s_{mno}\,, & m=1,2,3,\ n=1,2,3,\ o=4,5,6,\ n=o=4,5,6, \\ 8s_{ijklpq} & = & s_{mno}\,, & m=1,2,3,\ n=4,5,\ o=5,6, \\ 2s_{ijklpq} & = & s_{mno}\,, & m=4,5,6,\ n=o=1,2,3, \\ 4s_{ijklpq} & = & s_{mno}\,, & m=4,5,6,\ n\neq o,\ n=1,2,\ o=2,3, \\ 8s_{ijklpq} & = & s_{mno}\,, & m=4,5,6,\ n=1,2,3,\ o=4,5,6,\ n=o=4,5,6, \\ 16s_{ijklpq} & = & s_{mno}\,, & m=4,5,6,\ n=4,5,\ o=5,6. \end{array}$$

The equation

$$\varepsilon_{ij} = \frac{1}{2} s^{ET}_{ijklpq}\sigma_{kl}\sigma_{pq}\,, \qquad i,j,k,l,p,q = 1,2,3$$

can be written in the form

$$\varepsilon_m = \frac{1}{2} s_{mno}\sigma_n\sigma_o\,, \qquad m,n,o = 1,2,3,\ldots\,.$$

Considering equations (2.6), (2.7) and (2.8) we obtain in a non-linear approximation:

$$\left.\begin{array}{rcl} \varepsilon_{ij} & = & s_{ijkl}\sigma_{kl} + \frac{1}{2}s_{ijklpq}\sigma_{kl}\sigma_{pq} + \ldots\,, \\ D_m & = & d_{mkl}\sigma_{kl} + \frac{1}{2}d_{mklpq}\sigma_{kl}\sigma_{pq} + \ldots\,, \\ S & = & \alpha_{kl}\sigma_{kl} + \frac{1}{2}\alpha_{klpq}\sigma_{kl}\sigma_{pq} + \ldots \end{array}\right\} \qquad \text{if } E_n = 0,\ \Delta T = 0,$$

$$\left.\begin{array}{rcl} \varepsilon_{ij} & = & d_{nij}E_n + \frac{1}{2}o_{ijnt}E_nE_t + \ldots\,, \\ D_m & = & \varepsilon_{nm}E_n + \frac{1}{2}\varepsilon_{nmt}E_nE_t + \ldots\,, \\ S & = & p_nE_n + \frac{1}{2}p_{nt}E_nE_t + \ldots \end{array}\right\} \qquad \text{if } \sigma_{kl} = 0,\ \Delta T = 0,$$

$$\left.\begin{array}{rcl} \varepsilon_{ij} & = & \alpha_{ij}T + \frac{1}{2}r_{ij}TT + \ldots\,, \\ D_m & = & p_mT + \frac{1}{2}u_mTT + \ldots\,, \\ S & = & \xi T + \frac{1}{2}\rho TT + \ldots \end{array}\right\} \qquad \text{if } \sigma_{kl} = 0,\ E_n = 0.$$

An analogical matrix equation can be derived for non-linear effects (equations (2.6), (2.7) and (2.8)):

$$\begin{bmatrix} \varepsilon_{ij} \\ D_m \\ S \end{bmatrix} = \begin{bmatrix} A & D & E \\ D & B & F \\ E & F & C \end{bmatrix} \begin{bmatrix} \sigma_{kl} \\ E_n \\ T \end{bmatrix}, \tag{3.3}$$

where the basic effects are given by the following constants:

$$\begin{aligned}
A &= s^{E,T}_{ijkl} + \tfrac{1}{2} s^{E,T}_{ijklpq}\sigma_{pq} + \tfrac{1}{2} d^{T}_{ijkln}E_n + \tfrac{1}{2}\alpha^{E}_{ijkl}T,\\
B &= \varepsilon^{T,\sigma}_{nmt} + \tfrac{1}{2}\varepsilon^{T,\sigma}_{nmt}E_n + \tfrac{1}{2} o^{T}_{nmkl}\sigma_{kl} + \tfrac{1}{2} p^{\sigma}_{nm}T,\\
C &= \xi^{E,\sigma} + \tfrac{1}{2}\rho^{E,\sigma}T + \tfrac{1}{2}u^{\sigma}_{n}E_n + \tfrac{1}{2} r^{E}_{kl}\sigma_{kl}
\end{aligned}$$

and the conjugate effects are described by

$$\begin{aligned}
D &= d^{T}_{ijn} + \tfrac{1}{2} d^{T}_{klijn}\sigma_{kl} + \tfrac{1}{2} o^{T}_{ijnt}E_t + \tfrac{1}{2} k_{ijn}T,\\
E &= \alpha^{E}_{ij} + \tfrac{1}{2}\alpha^{E}_{ijkl}\sigma_{kl} + \tfrac{1}{2} r^{E}_{ij}T + \tfrac{1}{2} k_{ijn}E_n\,,\\
F &= p^{\sigma}_{m} + \tfrac{1}{2} p^{\sigma}_{mn}E_n + \tfrac{1}{2} k_{mkl}\sigma_{kl} + \tfrac{1}{2} u^{\sigma}_{m}T.
\end{aligned}$$

As we can see, the matrix of non-linear effects is also a symmetrical one.

4. Summary

Using the Gibbs function (G), the equations describing the physical quantities ε_{ij}, D_m, S have been derived for the non-linear effects of piezoelectric bodies. Relevant equations are included in section 3. It has been demonstrated that the relations between the material constants, which are tensors of zeroth to sixth order, can be written in non-linear approximation in the form of material equations where the elements of the matrices are the sums of appropriate matrices which represent the tensors (relation of (3.3)). The relations of (3.3) were used to derive the linear effects (relations of (3.2)).

The equations describing linear and non-linear phenomena for particular crystallographic point groups reduce because of monocrystal symmetry [5,6,12,13,14,15,16].

From the rewritten relations of (2.6, 2.7, 2.8) in the matrix notation (table 1) we can easily identify the interrelations of the tensor components, especially for separate physical effects. Further simplifications and decays of some components of higher order tensors may be obtained for appropriate point groups (crystal classes).

Table 1. Matrices of the coefficients (tensor components) in non-linear expansion.

	σ_n	$\sigma_n\sigma_o$	$E_n\sigma_o$	$\sigma_n T$	E_n	E_nE_t	E_nT	T	T^2
ε_m	s_{mn} 6×6	s_{mno} 6×21	d_{mno} 6×15	α_{mnl} 6×6	d_{nm} 6×3	o_{mnt} 6×6	k_{mn} 6×3	α_m 6×1	r_m 6×1
D_m	d_{mn} 3×6	d_{nmo} 3×21	o_{omn} 3×15	k_{nm} 3×6	ε_{mn} 3×3	ε_{mnt} 3×6	p_{nm} 3×3	p_m 3×1	u_m 3×1
S	α_n 1×6	α_{no} 1×21	k_{on} 1×15	r_n 1×6	p_n 1×3	p_{nt} 1×6	u_n 1×3	ξ 1×1	ρ 1×1

$$(6+3+1)\times(6+21+15+6+3+6+3+1+1) = 10\times 62$$

In 1952, with the aim to interpret the properties of the tetragonal antiferroelectric crystal $ND_4D_2PO_4$, Mason [10,11] made use of the elastic Gibbs function G_1 :

$$G_1 = U - \varepsilon_{ij}\sigma_{ij} - TS$$

in its differential form:

$$\mathrm{d}G_1 = -\varepsilon_{ij}\mathrm{d}\sigma_{kl} + E_n\mathrm{d}D_n - S\mathrm{d}T.$$

The equations and formulae describing ε_{ij}, E_n and S, which have been derived by Mason [10], depend on σ_{kl}, D_n and T. So it is not surprising that they differ from the equations presented in this paper (equations (2.6), (2.7) and (2.8)) both in linear and non-linear approximations. In our calculations we used a Gibbs function which had the form of G:

$$G = U - \varepsilon_{ij}\sigma_{kl} - E_nD_n - TS$$

and a differential form of

$$\mathrm{d}G = -\varepsilon_{ij}\mathrm{d}\sigma_{kl} - D_n\mathrm{d}E_n - S\mathrm{d}T.$$

The equations obtained for ε_{ij}, D_n and S depend on σ_{kl}, E_n and T. There is a definite sense in which our results differ from those achieved by Mason. For example, according to Mason (function G_1) [10] we have the following relations for the linear effects:

$$\begin{aligned}
\varepsilon_{ij} &= \left.\frac{\partial\varepsilon_{ij}}{\partial\sigma_{kl}}\right|_{D,T}\sigma_{kl} + \underline{\left.\frac{\partial\varepsilon_{ij}}{\partial D_m}\right|_{\sigma,T} D_m} + \left.\frac{\partial\varepsilon_{ij}}{\partial T}\right|_{\sigma,D} T,\\
E_n &= \underline{\left.\frac{\partial E_n}{\partial\sigma_{kl}}\right|_{D,T}\sigma_{kl}} + \underline{\left.\frac{\partial E_n}{\partial D_m}\right|_{\sigma,T} D_m} + \underline{\left.\frac{\partial E_n}{\partial T}\right|_{\sigma,D} T},\\
S &= \left.\frac{\partial S}{\partial\sigma_{kl}}\right|_{D,T}\sigma_{kl} + \underline{\left.\frac{\partial S}{\partial D_m}\right|_{\sigma,T} D_m} + \left.\frac{\partial S}{\partial T}\right|_{\sigma,D} T.
\end{aligned}$$

Our results (based on function G) take the form

$$\begin{aligned}
\varepsilon_{ij} &= \left.\frac{\partial\varepsilon_{ij}}{\partial\sigma_{kl}}\right|_{E,T}\sigma_{kl} + \underline{\left.\frac{\partial\varepsilon_{ij}}{\partial E_n}\right|_{\sigma,T} E_n} + \left.\frac{\partial\varepsilon_{ij}}{\partial T}\right|_{\sigma,E} T,\\
D_m &= \underline{\left.\frac{\partial D_m}{\partial\sigma_{kl}}\right|_{E,T}\sigma_{kl}} + \underline{\left.\frac{\partial D_m}{\partial E_n}\right|_{\sigma,T} E_n} + \underline{\left.\frac{\partial D_m}{\partial T}\right|_{\sigma,E} T},\\
S &= \left.\frac{\partial S}{\partial\sigma_{kl}}\right|_{E,T}\sigma_{kl} + \underline{\left.\frac{\partial S}{\partial E_n}\right|_{\sigma,T} E_n} + \left.\frac{\partial S}{\partial T}\right|_{\sigma,E} T.
\end{aligned}$$

Relevant differences have been underlined.

Considering the physical properties of the crystals, the symmetries of the tensor components and the order of differentiation of the thermodynamic function of state as a total differential, we can use a more concise matrix notation, e.g:

s_{ijkl}	$\rightarrow$	s_{mn}	$(m, n = 1, \ldots, 6)$, fourth-order tensor, second-order physical constant;
s_{ijklpq}	$\rightarrow$	s_{mno}	$(m, n, o = 1, \ldots, 6)$, sixth-order tensor, third-order physical constant;
d_{ijkln}	$\rightarrow$	d_{mno}	$(m, n = 1, \ldots, 6,\ o = 1, 2, 3)$, fifth-order tensor, third-order physical constant;
d_{nij}	$\rightarrow$	d_{nm}	$(n = 1, 2, 3,\ m = 1, \ldots, 6)$, third-order tensor, second-order physical constant;
o_{ijnt}	$\rightarrow$	o_{mnt}	$(m = 1, \ldots, 6,\ n, t = 1, 2, 3)$, fourth-order tensor, third-order physical constant;
α_{ij}	$\rightarrow$	α_m	$(m = 1, \ldots, 6)$, second-order tensor, second-order physical constant, etc.

During transition from tensor to matrix notation we neglected the coefficients that were different for relevant components (those for s_{ijkl} and s_{ijklpq} are listed in section 3).

Equally concise are the matrices of the coefficients (tensor components) in non-linear expansion. All of the coefficients (tensor components) incorporated in equations (2.6), (2.7) and (2.8), which occur on the right-hand side of table 1, are presented in the form of matrix 10×62:

$$(6 + 3 + 1) \times (6 + 21 + 15 + 6 + 3 + 6 + 3 + 1 + 1) = 10 \times 62.$$

For linear effects we have matrix 10×10:

$$(6 + 3 + 1) \times (6 + 3 + 1) = 10 \times 10.$$

Matrix notation is clear and very convenient, and in its external form it is similar for all (eight) thermodynamic functions, which have been used to describe the physical quantities for piezoelectric crystals. Making use of the data reported in the literature [1,3,5,13,14,15,16], we can establish the number of independent components of particular tensors for each point group, as well as define the relations between some elements of these matrices.

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Нелінійні механічні, електричні та термічні явища в п’єзоелектричних кристалах

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Отримано 25 серпня 2002 р., в остаточному вигляді – 31 березня 2003 р.

Механічні, електричні та термічні явища у п’єзоелектричних кристалах вивчаються у нелінійному наближенні. З цією метою використано термодинамічний потенціал, який описує анізотропне тіло. Розглянуто потенціал Гіббса. Розрахунки охоплюють тензор деформації $\varepsilon_{ij} = f(\sigma_{kl}, E_n, T)$, вектор індукції $D_m = f(\sigma_{kl}, E_n, T)$ та ентропію $S = f(\sigma_{kl}, E_n, T)$ як функцію механічного напруження σ_{kl}, величини поля E_n і різниці температур T. Отримано рівняння, які описують анізотропні п’єзоелектричні тіла, якщо відомі “сили” σ_{kl}, E_n, T, що діють на кристал.

Ключові слова: *п’єзоелектричні кристали, термодинаміка, анізотропні тіла, тензори*

PACS: *65.40.-b, 77.65.-j, 77.65.Bn, 77.65.Ly, 05.70.Ce*