Piezoelectricity and ferroelectricity Phenomena and properties

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What is the phenomenon about?

- Metallic membrane with ,,something strange"
- LEDs flash, why?





J.Erhart: Demonstrujeme piezoelektrický jev, Matematika, fyzika, informatika 20 (2010) 106-109

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History

- **1880, 1881** Pierre a Jacques Curie, discovery of piezoelectricity, tourmaline and quartz
- 1917 A.Langevin ultrasound generation, sonar
- **1921** ferroelectricity J.Valasek: Piezoelectricity and allied phenomena in Salt, Phys.Rev. 17 (1921) 475
- **1926** W.Cady frequency stabilization of oscillator circuit by the quartz resonator
- 1944-1946 USA, SSSR, Japonsko BaTiO₃ ferroelectric ceramics
- **1954** B.Jaffe et al PZT ceramics
- **60.** léta LiNbO₃ and LiTaO₃ single crystals
- 70.léta ferroelectric polymer PVDF
- 80.léta piezoelectric composites
- 90.léta domain engineering in PZN-PT, PMN-PT single crystals

Predecessors of piezoelectricity

Pyroelectricity

tourmaline = lapis electricus (Na,Ca)(Mg,Fe)₃B₃Al₆Si₆(O,OH,F)₃₁

Franz Ulrich Theodor Aepinus (1724 – 1802) – polar phenomenon

David Brewster – "pyroelectricity" 1824 pyros=oheň



Tourmaline crystal.



Carl Linnaeus (1707 – 1778)



David Brewster (1781 - 1868)

Pyroelectricity

A.C.Becquerel first pyroelectricity measurement 1828 William Thomson (Lord Kelvin) first pyroelectricity theory 1878, 1893



Antoine César Becquerel (1788 –1878)



$$\Delta P_S = p \cdot \Delta \theta$$

William Thomson, Lord Kelvin (1824 – 1907)

Piezoelectricity discovery

Tourmaline crystal, 1880



8.4.1880Société minéralogique de France24.8.1880Académie des Sciences

 $\Delta P = d \cdot T$

Curie J, Curie P (1880) Développement, par pression, de l'électricité polaire dans les cristaux hémièdres à faces inclinées. Comptes rendus de l'Académie des Sciences 91: 294; 383.

Curie J, Curie P (1881) Contractions et dilatations produites par des tensions électriques dans les cristaux hémièdres à faces inclinées. Comptes rendus de l'Académie des Sciences 93: 1137-1140.

Phenomenon properties

- Linear phenomenon, charge is independent from crystal length, it depends on the electrode area
- Phenomenon exists due to crystal anisotropy (polar axes), amorphous materials are not piezoelectric

Curie's principle

Symmetry elements of external field must be included in the phenomenon symmetry.

Crystal under the influence of external field exhibits only symmetry elements common to the symmetry of crystal itself and of the external field.

Example: mechanical pressure along [111] direction exerted on the cubic crystal with m3m symmetry causes symmetry reduction of deformed crystal to 3m symmetry class

Piezoelectricity

Direct phenomenonmechanical pressure \rightarrow electrical chargeConverse phenomenonelectric field \rightarrow mechanical deformation

It is limited to certain crystallographic symmetry classes (20 from 32 classes)

1, 2, *m*, 222, *mm*2, 4, $\overline{4}$, 422, 4*mm*, $\overline{4}2m$, 3, 32, 3*m*, 6, $\overline{6}$, 622, 6*mm*, $\overline{6}2m$, $\overline{4}3m$, 23 Example: SiO₂ (quartz) symmetry 32



Measurement technique

Direct phenomenon (Brothers Curie)

- Thompson's electrometer
- Null method $\Delta Q = V \Delta C$

(Daniel's cell – 1.12V, 1836)







Measurement technique

Converse phenomenon (Brothers Curie)

- Holtz's machine (induction electricity, HV)
- Strain measured by the direct effect, optically







Piezoelectricity origin

Brothers Curie – molecular theory



Charges generated at the compression (a) and tension (b) of quartz crystal basic unit

First theory and application of piezoelectricity

Tensor analysis developed for the crystal anisotropy description 1890 Woldemar Voigt: Lehrbuch der Kristallographie, Teubner Verlag 1910



Woldemar Voigt (1850 –1919)

First application – electrometer, radioactivity study (Maria Skłodowska-Curie)



Curie's electrometer



Maria Skłodowska-Curie (1867 – 1934)

Coupled field phenomena



Ferroelectricity

Joseph Valasek, 1920, Rochelle Salt NaKC₄H₄O₆.4H₂O



Hysteresis loop of Rochelle Salt - dry crystal, 0°C

Valasek J (1921) Piezoelectricity and allied phenomena in Rochelle salt. Phys. Rev. 17: 475-481

Electromechanical phenomena

Direct conversion between mechanical and electrical energy

- Linear effects Piezo- and Pyroelectricity
- Nonlinear effects Ferroelectricity, Electrostriction

Analogy in magnetic materials

• Piezomagnetic properties, magnetostriction, magnetoelectric effect, etc.

Crystallographic constraints for piezoelectricity

Noncentrosymmetric classes (except of 432) 20 piezoelectric crystallographic classes

- Polar classes (10) singular polar axis
 1, 2, m, mm2, 4, 4mm, 3, 3m, 6, 6mm
- Polar-neutral classes (10) multiple polar axes 222, $\overline{4}$, 422, $\overline{4}2m$, 32, $\overline{6}$, 622, $\overline{6}m2$, $\overline{4}3m$, 23

Equations of state

Example: piezoelectricity

$$S_{\mu} = s_{\mu\nu}^{E} T_{\nu} + d_{k\mu} E_{k}$$
$$D_{i} = d_{i\nu} T_{\nu} + \varepsilon_{ik}^{T} E_{k}$$

$$S_{\mu} = s_{\mu\nu}^{D} T_{\nu} + g_{k\mu} D_{k}$$
$$E_{i} = -g_{i\nu} T_{\nu} + \beta_{ik}^{T} D_{k}$$

$$T_{\mu} = c_{\mu\nu}^{E} S_{\nu} - e_{k\mu} E_{k}$$
$$D_{i} = e_{i\nu} S_{\nu} + \varepsilon_{ik}^{S} E_{k}$$

$$T_{\mu} = c_{\mu\nu}^{D} S_{\nu} - h_{k\mu} D_{k}$$
$$E_{i} = -h_{i\nu} S_{\nu} + \beta_{ik}^{S} D_{k}$$

Piezoelectric coefficients

Different coefficients due to the choice of independent variables

$$d_{i\mu} = \frac{\partial D_i}{\partial T_{\mu}} = \frac{\partial S_{\mu}}{\partial E_i} \qquad C N^{-1}$$
$$g_{i\mu} = -\frac{\partial E_i}{\partial T_{\mu}} = \frac{\partial S_{\mu}}{\partial D_i} \qquad C^{-1} m^2$$

$$h_{i\mu} = -\frac{\partial E_i}{\partial S_{\mu}} = -\frac{\partial T_{\mu}}{\partial D_i}$$
 $C^{-1} N$

$$e_{i\mu} = \frac{\partial D_i}{\partial S_{\mu}} = -\frac{\partial T_{\mu}}{\partial E_i}$$
 C m⁻²

Material property anisotropy d₃₃ surface

 $P_{S}[001]_{T}$





 $PbTiO_3 - 4mm$

 $\begin{array}{l} d_{33}l_3{}^3 + (d_{31} + d_{15})l_3(l_1{}^2 + l_2{}^2) \\ l_1 = \sin(\theta) \cos(\phi), \ l_2 = \sin(\theta) \sin(\phi), \ l_3 = \cos(\theta) \\ d_{33} = 83.7, \ d_{31} = -27.2, \ d_{15} = 60.2 \ [pC/N] \end{array}$

Maximum 83.7pC/N for $\theta = 0^{\circ}$, i.e. $[001]_{C}$

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Material property anisotropy d₃₃ surface

 $P_{S}[001]_{T}$





 $BaTiO_3 - 4mm$

 $\begin{aligned} &d_{33}l_3^3 + (d_{31} + d_{15})l_3(l_1^2 + l_2^2) \\ &l_1 = \sin(\theta)\cos(\phi), \ l_2 = \sin(\theta)\sin(\phi), \ l_3 = \cos(\theta) \\ &d_{33} = 90, \ d_{31} = -33.4, \ d_{15} = 564 \ [pC/N] \end{aligned}$

Maximum 224pC/N for $\theta = 51^{\circ}$ 90pC/N for [001]_C 221pC/N for [111]_C

Pyroelectricity

Direct effect

Temperature change \rightarrow electric charge **Converse effect** (electrocaloric effect) Electric field \rightarrow heat generation or absorption Anisotropy

Example: Lithium tetraborate $Li_2B_4O_7$, symmetry *4mm*



Crystallographic constraints for pyroelectricity

Polar symmetry classes (10) – singular polar axis

1, 2, *m*, *mm*2, 4, 4*mm*, 3, 3*m*, 6, 6*mm*

Pyroelectric polarization of material (dipole moment) – polar axis direction

Electrostriction



• No constraints on the material symmetry, effect exists in all materials

Electrostriction

Nonlinear equations of state

$$S_{ij} = d_{kij}E_k + Q_{ijkl}P_kP_l$$

Without crystallographic limits! All materials exhibit electrostrictive properties

Electrostriction in cubic materials

Electrostrictive coefficients Q_{11} , Q_{12} , Q_{44}



Ferroelectricity

Spontaneous dipole moments = pyroelectricity with switchable polarization Electric analogy of permanent magnets

Characteristic properties

- Ferroelectric domains and domain walls
- Hysteresis loop D-E (S-E)

Hierarchy of electromechanical phenomena



Ferroelectricity

Spontaneous existence of polarization (and spontaneous strain at the same time)

- structural phase transition
- Ferroelectric/ferroelastic domains
- orientation domain states
- Domain walls
- Hysteresis

BaTiO₃ – paraelectric phase

Perovskite structure



BaTiO₃ – ferroelectric phase

Several orientation states exist for the spontaneous polarization





Domains, domain walls

- **Domain** space continuous region with the same orientation of the spontaneous dipole moment (polarization)
- **Domain walls** interfaces between domains
- Charged walls
- Neutral walls

Ferroelectric domains exist in ferroelectric phase Phase transition – Curie temperature T_C

D-E a S-E hysteresis loops



Fig. 5 Polarization and strain response of PZN-4.5%PT single crystals under electric field in directions 10°, 25°, and 35° off <001>. a Strain versus electric field; b electric displacement versus electric field

T. Liu, C. S. Lynch: Domain engineered relaxor ferroelectric single crystals Continuum Mech. Thermodyn. **18** (2006) 119–135

Remanent polarization





Mechanism of domain reorientation



Remanent deformation

Ferroelasticity in ferroelectric materials

$$\begin{split} \mathbf{S}_{3}^{\mathbf{pr}} &= 2 \ Q_{33}^{*} P_{\mathbf{r}} P_{3} = g_{33} P_{3}, \\ \mathbf{g}_{33} &= 2 \ Q_{33}^{*} P_{\mathbf{r}}, \end{split}$$

 $S_3^{pr} = strain at constant remanent polarisation P_r$.

strain S3=Sr+Sm

under electric field

E,P

$$d_{33} = \epsilon^{T}{}_{33} g_{33}, d_{33} = 2 Q_{33} \epsilon^{T}{}_{33} P_{r}.$$



S3' ‰

P_r

Sm

S,

Domains in BaTiO₃ ceramics $m\overline{3}m \rightarrow 4mm$





- Domain structure evolution during heating of BaTiO₃ ceramics over the Curie temperature
- (a) Temperature gradient parallel to the domain walls
- (b) Temperature gradient perpendicular to the domain walls

Sang-Beom Kim, Doh-Yeon Kim: J. Am. Ceram. Soc., 83 [6] 1495–98 (2000)

Domains in BaTiO₃ ceramics $m\overline{3}m \rightarrow 4mm$





Etched surface of BaTiO₃ ceramics

- a) Herringbone and chessboard pattern
- b) Band structure of DW's, domains continuously cross the grain boundaries

G.Arlt, P.Sasko: J.Appl.Phys. 51 (1980) 4956-4960

Ferroic phases

Structural phase transitions Parent phase (e.g. paraelectric) \rightarrow ferroic phase

Feroelectrics LiNbO₃ $3m \rightarrow 3m$ KNbO₃ $m\overline{3}m \rightarrow mm2$ BaTiO₃ $m\overline{3}m \rightarrow 4mm$ Pb₅Ge₃O₁₁ $\overline{6} \rightarrow 3$ KIO₃ $3m \rightarrow m$

Ferroelastics AgNbO₃ NaNbO₃ $m\overline{3}m \rightarrow mmm$ Pb₃(PO₄)₂ $\overline{3}m \rightarrow 2/m$

Material property anomalies

Dielectric permittivity, spontaneous polarization, etc.



Material property anomalies

Piezoelectric coefficient LiTaO₃



Landau-Ginzburg-Devonshire theory

Power expansion of thermodynamic potential $\Phi(\boldsymbol{T},\boldsymbol{\eta}) = \Phi_0 + \frac{1}{2}\alpha(\boldsymbol{T} - \boldsymbol{T}_C)\boldsymbol{\eta}^2 + \frac{1}{4}\beta\boldsymbol{\eta}^4$ Equilibrium and stability $\frac{\partial \Phi}{\partial \eta} = 0, \frac{\partial^2 \Phi}{\partial n^2} > 0$ Equilibrium phase transition parameter value $\frac{\partial \Phi}{\partial \eta} = \alpha (T - T_C) \eta_0 + \beta \eta_0^3 = 0 \qquad \eta_0 = \begin{cases} 0 & T > T_C \\ \pm \left(-\frac{\alpha (T - T_C)}{\beta} \right)^{1/2} & T < T_C \end{cases}$

2nd order phase transition



1st order phase transition



Curie – Weiss law

Dielectric permittivity temperature dependence



Spontaneous strain vs. spontaneous polarization

Generally (for normal ferroelectrics) $S_{kl} = Q_{ijkl}P_iP_j$

Example for the ferroelectric species $4/mm \rightarrow m_{xy}$

$$\begin{pmatrix} S_1 \\ S_2 \\ S_3 \\ S_4 \\ S_5 \\ S_6 \end{pmatrix} = \begin{pmatrix} Q_{11} & Q_{12} & Q_{13} & 0 & 0 & 0 \\ Q_{12} & Q_{11} & Q_{13} & 0 & 0 & 0 \\ Q_{31} & Q_{31} & Q_{33} & 0 & 0 & 0 \\ 0 & 0 & 0 & Q_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & Q_{44} & 0 \\ 0 & 0 & 0 & 0 & 0 & Q_{66} \end{pmatrix} \begin{pmatrix} P_{S1}^2 \\ P_{S1}^2 \\ P_{S3}^2 \\ P_{S1}^2 \\ P_{S3}^2 \\ P_{S1}P_{S3} \\ P_{S1}P_{S3} \\ P_{S1}^2 \end{pmatrix}$$

 $P_{S} = (P_{S1}, P_{S1}, P_{S3})$

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Experimental characterization of spontaneous deformation





Lattice constants measured by X-Ray diffraction

- In parent phase (extrapolation down to the ferroic phase)
- In ferroic phase

General formula for the components of strain tensor

J.L.Schlenker, G.V.Gibbs, M.B.Boisen, Jr.: Acta Cryst. A34 (1978) 52-54

$Bi_4Ti_3O_{12}$

 $4 / mmm \rightarrow m_{xy}$

8 ferroelectric DS4 ferroelastic DS



 $P_a >> P_c$

Bi₄Ti₃O₁₂

Spontaneous deformation/polarization (components in the parent phase coordinate system)

$$S^{(1)} = \begin{pmatrix} S_{11} & S_{12} & S_{13} \\ S_{12} & S_{11} & -S_{13} \\ S_{13} & -S_{13} & S_{33} \end{pmatrix} P^{I} = (\frac{1}{\sqrt{2}}P_{a}, -\frac{1}{\sqrt{2}}P_{a}, P_{c}) P^{II} = (-\frac{1}{\sqrt{2}}P_{a}, \frac{1}{\sqrt{2}}P_{a}, -P_{c}) \\ S^{(2)} = \begin{pmatrix} S_{11} & -S_{12} & S_{13} \\ -S_{12} & S_{11} & S_{13} \\ S_{13} & S_{13} & S_{33} \end{pmatrix} P^{III} = (\frac{1}{\sqrt{2}}P_{a}, \frac{1}{\sqrt{2}}P_{a}, P_{c}) P^{IV} = (-\frac{1}{\sqrt{2}}P_{a}, -\frac{1}{\sqrt{2}}P_{a}, -P_{c}) \\ S^{(3)} = \begin{pmatrix} S_{11} & S_{12} & -S_{13} \\ S_{12} & S_{11} & S_{13} \\ -S_{13} & S_{13} & S_{33} \end{pmatrix} P^{V} = (-\frac{1}{\sqrt{2}}P_{a}, \frac{1}{\sqrt{2}}P_{a}, P_{c}) P^{VI} = (\frac{1}{\sqrt{2}}P_{a}, -\frac{1}{\sqrt{2}}P_{a}, -P_{c}) \\ S^{(4)} = \begin{pmatrix} S_{11} & -S_{12} & -S_{13} \\ -S_{12} & S_{11} & -S_{13} \\ -S_{13} & -S_{13} & S_{33} \end{pmatrix} P^{VII} = (-\frac{1}{\sqrt{2}}P_{a}, -\frac{1}{\sqrt{2}}P_{a}, P_{c}) P^{VIII} = (\frac{1}{\sqrt{2}}P_{a}, \frac{1}{\sqrt{2}}P_{a}, -P_{c}) \\ P^{VIII} = (-\frac{1}{\sqrt{2}}P_{a}, -\frac{1}{\sqrt{2}}P_{a}, P_{c}) P^{VIII} = (\frac{1}{\sqrt{2}}P_{a}, \frac{1}{\sqrt{2}}P_{a}, -P_{c}) \\ P^{VIII} = (-\frac{1}{\sqrt{2}}P_{a}, -\frac{1}{\sqrt{2}}P_{a}, P_{c}) P^{VIII} = (\frac{1}{\sqrt{2}}P_{a}, \frac{1}{\sqrt{2}}P_{a}, -P_{c}) \\ P^{VIII} = (-\frac{1}{\sqrt{2}}P_{a}, -\frac{1}{\sqrt{2}}P_{a}, P_{c}) P^{VIII} = (-\frac{1}{\sqrt{2}}P_{a}, -\frac{1}{\sqrt{2}}P_{a}, -P_{c}) \\ P^{VIII} = (-\frac{1}{\sqrt{2}}P_{a}, -\frac{1}{\sqrt{2}}P_{a}, -P_{c}) P^{VIII} = (-\frac{1}{\sqrt{2}}P_{a}, -\frac{1}{\sqrt{2}}P_{a}, -P_{c}) P^{VIII} = (-\frac{1}{\sqrt{2}}P_{a}, -P_{c}) P^{VIII} = (-\frac{1}{\sqrt{2}}$$

Domain wall orientation

$$(ds^{(2)})^2 - (ds^{(1)})^2 = (S_{ij}^{(2)} - S_{ij}^{(1)})ds_i ds_j = \mathbf{0}$$

Example for $Bi_4Ti_3O_{12}$ Domain state pair $S^{(1)}$ (P⁽¹⁾, P⁽²⁾) and $S^{(2)}$ (P⁽³⁾,P⁽⁴⁾)

$$(ds_1 - \frac{S_{13}}{S_{12}}ds_3)ds_2 = \mathbf{0}$$

Two perpendicular domain wallsCharged wall(010)W-wallNeutral wall(10K)S-wall

$$K = -\frac{S_{13}}{S_{12}}$$

Domain wall orientations in Bi₄Ti₃O₁₂

	S ⁽¹⁾	S ⁽²⁾	S ⁽³⁾	S ⁽⁴⁾
	$P^{(1)}, P^{(2)}$	P ⁽³⁾ ,P ⁽⁴⁾	P ⁽⁵⁾ ,P ⁽⁶⁾	P ⁽⁷⁾ ,P ⁽⁸⁾
S ⁽¹⁾	N/A	(010)	(1-10)	(100)
$P^{(1)}, P^{(2)}$		(10 - K)	(001)	(01K)
S ⁽²⁾		N/A	(100)	(110)
$P^{(3)}, P^{(4)}$			(01 - K)	(001)
S ⁽³⁾			N/A	(010)
$P^{(5)}, P^{(6)}$				(10K)
S ⁽⁴⁾				N/A
P ⁽⁷⁾ ,P ⁽⁸⁾				

Domain wall types

W-walls

- W_{∞} arbitrary wall orientation
- W_f fixed crystallographic domain wall orientation

S-walls ("strange" walls, W'-walls)

- $S_1 P_S$ direction
- $S_2 b_{ijk}$ and Q_{ijkl}
- $S_3 P_S$ direction, b_{ijk} and Q_{ijkl}
- $S_4 P_S$ direction and magnitude, b_{ijk} and Q_{ijkl}
- $S_5 P_S$ magnitude, b_{ijk} and Q_{ijkl}

Permissible domain wall pairs

- W_{∞} arbitrary domain wall orientation $W_f W_f$ – fixed domain wall orientation $W_f S$ – fixed and ,,strange" walls
- SS pair of "strange" walls
- R walls are not permissible

J.Fousek, V.Janovec: J.Appl.Phys. **40** (1969) 135 J.Sapriel: Phys.Rev. **B12** (1975) 5128 J.Erhart: Phase Transitions **77** (2004) 989-1074

Antiferroelectricity

Dipole moments are partially compensated Switching possible at higher fields





Electromechanical coupling coefficient

Energy transfer efficiency between mechanical and electrical energy via piezoelectric effect

 $k^2 = \frac{\text{electrical energy converted to mechanical energy}}{\text{input electrical energy}}$

 $k^2 = \frac{\text{mechanical energy converted to electrical energy}}{\text{input mechanical energy}}$

Electromechanical coupling



Fig. 18.2. Diagram showing a conversion cycle of mechanical to electrical energy to illustrate the relation between the electromechanical coupling factor k_{33} and d_{33} , ε_{33}^{T} , and s_{33}^{E}

W.Heywang, K.Lubitz, W.Wersing (edts.): Piezoelectricity, Springer Verlag 2008

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Electromechanical coupling coefficients

Different modes

Transversal

$$k_{31}^2 = \frac{d_{31}^2}{s_{11}^E \varepsilon_{33}^T}$$

thickness-shear

$$k_{15}^2 = \frac{d_{15}^2}{s_{55}^E \varepsilon_{11}^T}$$

thickness

radial

$$k_t^2 = \frac{e_{33}^2}{c_{33}^D \varepsilon_{33}^S}$$

$$k_p^2 = \frac{2d_{31}^2}{\varepsilon_{33}^T(s_{11}^E + s_{12}^E)}$$

Dielectric losses

Permittivity – complex values $\mathcal{E} = \mathcal{E}' - j\mathcal{E}'' \quad \tan(\delta) = \frac{\mathcal{E}''}{\mathcal{E}'}$ Dissipated power = energy loss during 1s

$$P = U \cdot I = Z_C I^2 = \frac{C'' I^2}{\omega (C'^2 + C''^2)} - j \frac{C' I^2}{\omega (C'^2 + C''^2)}$$
$$C = (\varepsilon' - j\varepsilon'') \frac{S}{d} = C' - jC''$$
$$Z_C = \frac{1}{j\omega C} = \frac{C'' - jC'}{\omega (C'^2 + C''^2)}$$

Mechanical losses

Elastic properties – complex compliance

$$s = s' - js''$$

Mechanical quality $Q_{\rm m}$

$$Q_m = \frac{1}{2\pi f_m |Z| C^T k_{eff}^2}$$

Young's modulus and elastic coefficients

Examples for 4mm symmetry

Mechanical pressure

 $T_{11} = c_{11}S_{11} + c_{12}S_{22} + c_{13}S_{33}$ $T_{22} = c_{12}S_{11} + c_{11}S_{22} + c_{13}S_{33}$ $T_{33} = c_{13}S_{11} + c_{13}S_{22} + c_{33}S_{33}$ Mechanical deformation



Young's modulus



$$Y_{33} = c_{33} - \frac{2c_{13}^2}{c_{11} + c_{12}}$$

$$Y_{11} = \frac{(c_{11} - c_{12})[c_{33}(c_{11} + c_{12}) - 2c_{13}^2]}{c_{11}c_{33} - c_{13}^2}$$

Thank you for your attention!

