Internal energy in an electric field

In an electric field, if the dipole moment is changed, the change of the energy is,

$$\Delta U = \vec{E} \cdot \Delta \vec{P}$$

Using Einstein notation

$$dU = E_k dP_k$$

This is part of the total derivative of U

$$dU = TdS + \sigma_{ij} d\varepsilon_{ij} + E_k dP_K + H_l dM_l$$

Make a Legendre transformation to the Gibbs potential $G(T, H, E, \sigma)$

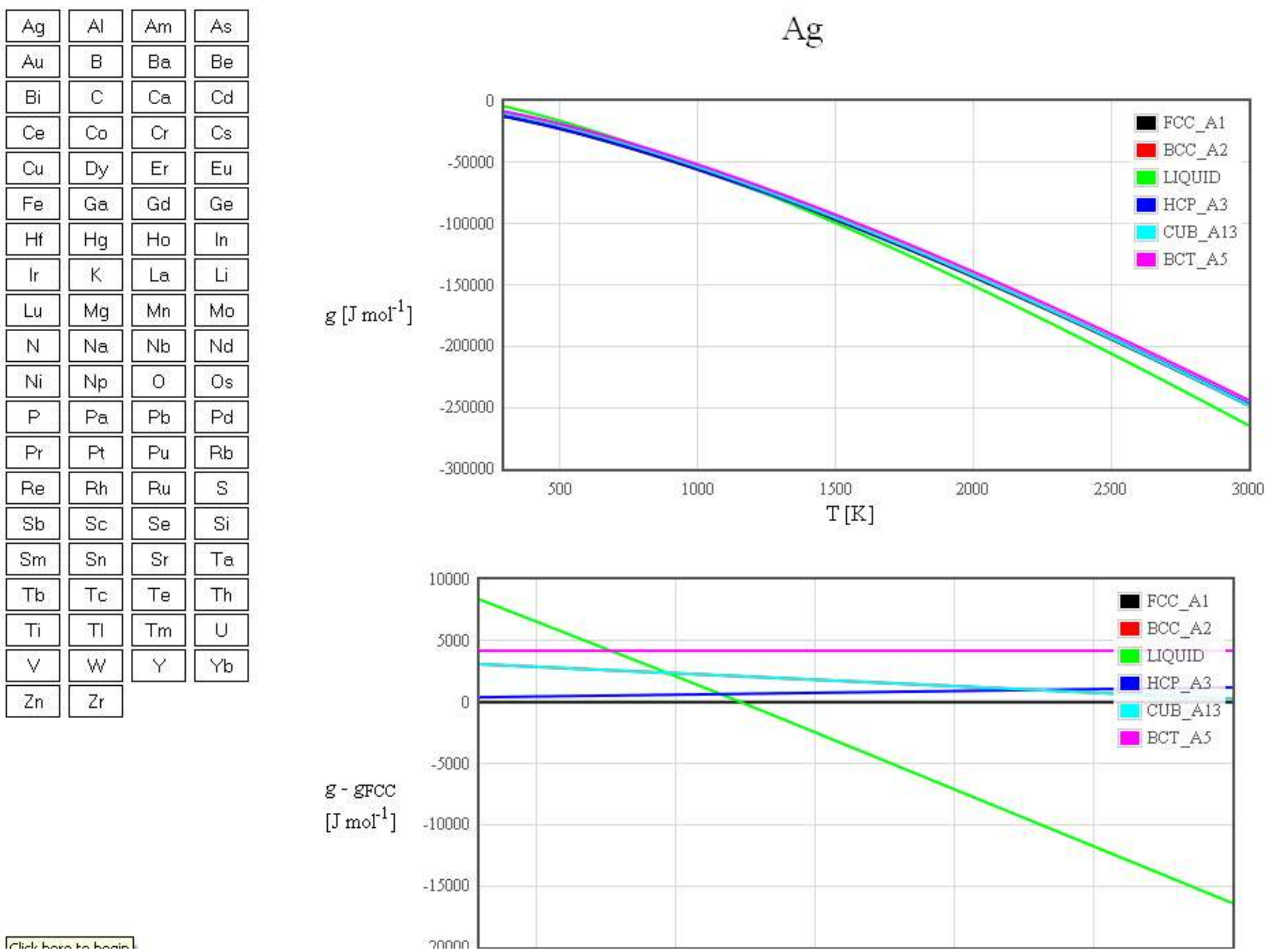
$$G = U - TS - \sigma_{ij}\varepsilon_{ij} - E_k P_K - H_l M_l$$

SGTE data for pure elements

SGTE thermodynamic data

The Scientific Group Thermodata Europe SGTE maintains thermodynamic databanks for inorganic and metallurgical systems. Data from their 'pure element database' is plotted below.

Typically, experiments are performed at constant pressure p, temperature T, and number N. Under these conditions, the system will go to the minimum of the Gibbs energy $G = U + pV - TS$. Here U is the internal energy, V is the volume, and S is the entropy. The top plot is the Gibbs energy per mole $g = u + pv - Ts$, where u is the internal energy per mole, v is the volume per mole, and s is the entropy per mole.



http://www.sciencedirect.com/science/article/pii/036459169190030N

Gibbs free energy

$$G = U - TS - \sigma_{ij}\varepsilon_{ij} - E_k P_K - H_l M_l$$

$$dG = dU - TdS - SdT - \sigma_{ij} d\varepsilon_{ij} - \varepsilon_{ij} d\sigma_{ij} - E_k dP_k - P_k dE_k - H_l dM_l - M_l dH_l$$

$$dU = TdS + \sigma_{ij} d\varepsilon_{ij} + E_k dP_K + H_l dM_l$$

$$dG = -SdT - \varepsilon_{ij} d\sigma_{ij} - P_k dE_k - M_l dH_l$$

total derivative: $dG = \left(\frac{\partial G}{\partial T}\right) dT + \left(\frac{\partial G}{\partial \sigma_{ij}}\right) d\sigma_{ij} + \left(\frac{\partial G}{\partial E_k}\right) dE_k + \left(\frac{\partial G}{\partial H_l}\right) dH_l$

$$\left(\frac{\partial G}{\partial \sigma_{ij}}\right) = -\varepsilon_{ij} \qquad \left(\frac{\partial G}{\partial E_k}\right) = -P_k$$

$$\left(\frac{\partial G}{\partial H_l}\right) = -M_l \qquad \left(\frac{\partial G}{\partial T}\right) = -S$$

$$d\varepsilon_{ij} = \underset{1}{\left(\frac{\partial \varepsilon_{ij}}{\partial \sigma_{kl}}\right)} d\sigma_{kl} + \underset{2}{\left(\frac{\partial \varepsilon_{ij}}{\partial E_k}\right)} dE_k + \underset{3}{\left(\frac{\partial \varepsilon_{ij}}{\partial H_l}\right)} dH_l + \underset{4}{\left(\frac{\partial \varepsilon_{ij}}{\partial T}\right)} dT$$

$$dP_i = \underset{5}{\left(\frac{\partial P_i}{\partial \sigma_{kl}}\right)} d\sigma_{kl} + \underset{6}{\left(\frac{\partial P_i}{\partial E_k}\right)} dE_k + \underset{7}{\left(\frac{\partial P_i}{\partial H_l}\right)} dH_l + \underset{8}{\left(\frac{\partial P_i}{\partial T}\right)} dT$$

$$dM_i = \underset{9}{\left(\frac{\partial M_i}{\partial \sigma_{kl}}\right)} d\sigma_{kl} + \underset{10}{\left(\frac{\partial M_i}{\partial E_k}\right)} dE_k + \underset{11}{\left(\frac{\partial M_i}{\partial H_l}\right)} dH_l + \underset{12}{\left(\frac{\partial M_i}{\partial T}\right)} dT$$

$$dS = \underset{13}{\left(\frac{\partial S}{\partial \sigma_{kl}}\right)} d\sigma_{kl} + \underset{14}{\left(\frac{\partial S}{\partial E_k}\right)} dE_k + \underset{15}{\left(\frac{\partial S}{\partial H_l}\right)} dH_l + \underset{16}{\left(\frac{\partial S}{\partial T}\right)} dT$$

1. Elastic deformation.
2. Reciprocal (or converse) piezo-electric effect.
3. Reciprocal (or converse) piezo-magnetic effect.
4. Thermal dilatation.
5. Piezo-electric effect.
6. Electric polarization.
7. Magneto-electric polarization.
8. Pyroelectricity.
9. Piezo-magnetic effect.
10. Reciprocal (or converse) magneto-electric polarization.
11. Magnetic polarization.
12. Pyromagnetism.
13. Piezo-caloric effect.
14. Electro-caloric effect.
15. Magneto-caloric effect.
16. Heat transmission.

Direct and reciprocal effects (Maxwell relations)

$$-\left(\frac{\partial^2 G}{\partial \sigma_{ij} \partial E_k}\right) = \left(\frac{\partial P_k}{\partial \sigma_{ij}}\right) = -\left(\frac{\partial^2 G}{\partial E_k \partial \sigma_{ij}}\right) = \left(\frac{\partial \varepsilon_{ij}}{\partial E_k}\right) = d_{kij}$$

$$-\left(\frac{\partial^2 G}{\partial \sigma_{ij} \partial H_l}\right) = \left(\frac{\partial M_l}{\partial \sigma_{ij}}\right) = -\left(\frac{\partial^2 G}{\partial H_l \partial \sigma_{ij}}\right) = \left(\frac{\partial \varepsilon_{ij}}{\partial H_l}\right) = q_{lij}$$

$$-\left(\frac{\partial^2 G}{\partial E_k \partial H_l}\right) = \left(\frac{\partial M_l}{\partial E_k}\right) = -\left(\frac{\partial^2 G}{\partial H_l \partial E_k}\right) = \left(\frac{\partial P_k}{\partial H_l}\right) = \lambda_{lk}$$

$$-\left(\frac{\partial^2 G}{\partial \sigma_{ij} \partial T}\right) = \left(\frac{\partial S}{\partial \sigma_{ij}}\right) = -\left(\frac{\partial^2 G}{\partial T \partial \sigma_{ij}}\right) = \left(\frac{\partial \varepsilon_{ij}}{\partial T}\right) = \alpha_{ij}$$

$$-\left(\frac{\partial^2 G}{\partial T \partial E_k}\right) = \left(\frac{\partial P_k}{\partial T}\right) = -\left(\frac{\partial^2 G}{\partial E_k \partial T}\right) = \left(\frac{\partial S}{\partial E_k}\right) = p_k$$

$$-\left(\frac{\partial^2 G}{\partial T \partial H_l}\right) = \left(\frac{\partial M_l}{\partial T}\right) = -\left(\frac{\partial^2 G}{\partial H_l \partial T}\right) = \left(\frac{\partial S}{\partial H_l}\right) = m_l.$$

Useful to check for errors in experiments or calculations

Maxwell relations

$$+\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V = \frac{\partial^2 U}{\partial S \partial V}$$

$$+\left(\frac{\partial T}{\partial P}\right)_S = +\left(\frac{\partial V}{\partial S}\right)_P = \frac{\partial^2 H}{\partial S \partial P}$$

$$+\left(\frac{\partial S}{\partial V}\right)_T = +\left(\frac{\partial P}{\partial T}\right)_V = -\frac{\partial^2 F}{\partial T \partial V}$$

$$-\left(\frac{\partial S}{\partial P}\right)_T = +\left(\frac{\partial V}{\partial T}\right)_P = \frac{\partial^2 G}{\partial T \partial P}$$

Useful to check for errors in experiments or calculations

Tensor properties of solids

Ohm's law

$$j_i = \sigma_{ij} E_j$$

Electric susceptibility

$$P_i = \chi_{ij} E_j$$

Seebeck effect

$$E_i = s_{ij} \nabla T_j$$

Thermal conductivity

$$J_i = -K_{ij} \nabla T_j$$

Piezoelectric effect

$$P_i = d_{ijk} \sigma_{jk}$$

Hall effect

$$E_i = R_{ijk} j_j B_k$$

Stiffness tensor

$$\varepsilon_{ij} = s_{ijkl} \sigma_{kl}$$

Piezoresistivity

$$\rho_{ij} = g_{ijkl} \sigma_{kl}$$

Electrostriction

$$\epsilon_{ij} = Q_{ijkl} E_k E_l$$

$$\epsilon_{ij} = d_{ijk} E_k + Q_{ijkl} E_k E_l + \cdots$$

Point Groups

Crystals can have symmetries: rotation, reflection, inversion,...

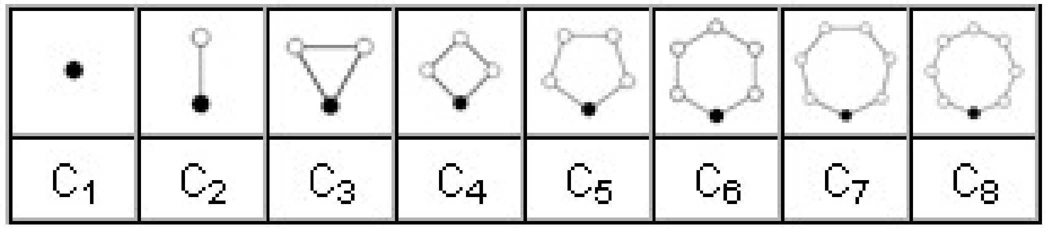
$$\begin{pmatrix} x' \\ y' \\ z' \end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & \cos\alpha & \sin\alpha \\ 0 & -\sin\alpha & \cos\alpha \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix}$$

Symmetries can be represented by matrices.
All such matrices that bring the crystal into itself form the group of the crystal.

$$\mathrm{AB} \in \mathrm{G} \text{ for } \mathrm{A}, \mathrm{B} \in \mathbf{G}$$

32 point groups (one point remains fixed during transformation)
230 space groups

Cyclic groups



C_2

$$E = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}, C_2 = \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

C_4

$$E = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}, C_4 = \begin{bmatrix} 0 & -1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{bmatrix}, C_2 = \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix}, C_4^3 = \begin{bmatrix} 0 & 1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

$$E = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}, C_6 = \begin{bmatrix} \frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 \\ \frac{\sqrt{3}}{2} & \frac{1}{2} & 0 \\ 0 & 0 & 1 \end{bmatrix}, C_3 = \begin{bmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{bmatrix}, C_2 = \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix}, {C_3}^2 = \begin{bmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} & 0 \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{bmatrix}, {C_6}^5 = \begin{bmatrix} \frac{1}{2} & \frac{\sqrt{3}}{2} & 0 \\ -\frac{\sqrt{3}}{2} & \frac{1}{2} & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

http://en.wikipedia.org/wiki/Cyclic_group

Pyroelectricity $\pi_i = -\left(\frac{\partial^2 G}{\partial E_i \partial T}\right)$

Pyroelectricity is described by a rank 1 tensor

$$\pi_i = \frac{\partial P_i}{\partial T}$$

$$\begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{bmatrix} \begin{bmatrix} \pi_x \\ \pi_y \\ \pi_z \end{bmatrix} = \begin{bmatrix} \pi_x \\ \pi_y \\ -\pi_z \end{bmatrix} \Rightarrow \begin{bmatrix} \pi_x \\ \pi_y \\ 0 \end{bmatrix}$$

$$\begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{bmatrix} \begin{bmatrix} \pi_x \\ \pi_y \\ \pi_z \end{bmatrix} = \begin{bmatrix} -\pi_x \\ -\pi_y \\ -\pi_z \end{bmatrix} \Rightarrow \begin{bmatrix} 0 \\ 0 \\ 0 \end{bmatrix}$$

Pyroelectricity

Quartz, ZnO, $LaTaO_3$

example
Turmalin: point group 3m
for $\Delta T = 1°C$,
$\Delta E \sim 7 \cdot 10^4$ V/m

Pyroelectrics have a spontaneous polarization. If it can be reversed by an electric field they are called Ferroelectrics ($BaTiO_3$)

Pyroelectrics are at Joanneum research to make infrared detectors (to detect humans).

10 Pyroelectric crystal classes: 1, 2, m, mm2, 3, 3m, 4, 4mm, 6, 6mm

Electric susceptibility $\chi_{ij} = -\left(\frac{\partial^2 G}{\partial E_i \partial E_j}\right)$

$$P_i = \chi_{ij} E_j$$

$$\begin{bmatrix} P_x \\ P_y \\ P_z \end{bmatrix} = \begin{bmatrix} \chi_{xx} & \chi_{xy} & \chi_{xz} \\ \chi_{yx} & \chi_{yy} & \chi_{yz} \\ \chi_{zx} & \chi_{zy} & \chi_{zz} \end{bmatrix} \begin{bmatrix} E_x \\ E_y \\ E_z \end{bmatrix}$$

Transforming P and E by a crystal symmetry must leave the susceptibility tensor unchanged

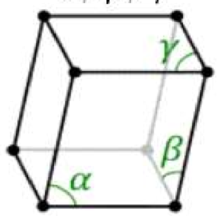
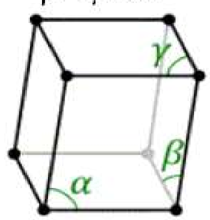
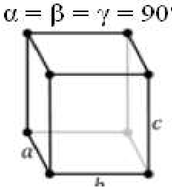
$$U\vec{P} = \chi U\vec{E} \qquad U^{-1}U\vec{P} = U^{-1}\chi U\vec{E} \qquad \chi = U^{-1}\chi U$$

If rotation by 180 about the z axis is a symmetry,

$$U = \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \qquad U^{-1} = U = \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \qquad U^{-1}\chi U = \begin{bmatrix} \chi_{xx} & \chi_{xy} & -\chi_{xz} \\ \chi_{yx} & \chi_{yy} & -\chi_{yz} \\ -\chi_{zx} & -\chi_{zy} & \chi_{zz} \end{bmatrix}$$

$$\chi_{xz} = \chi_{yz} = \chi_{zx} = \chi_{zy} = 0$$

The 32 Crystal Classes

Crystal system	Crystal Class	International symbol	Schoenflies symbol	Space groups	2-fold axes	3-fold axes	4-fold axes	6-fold axes	mirror planes	inversion	Examples	N sy el
Triclinic $a \neq b \neq c$ $\alpha \neq \beta \neq \gamma$ 	triclinic-pedial	1	C_1	1	-	-	-	-	-	n		
	triclinic-pinacoidal	$\bar{1}$	$S_2 = C_i$	2	-	-	-	-	-	y		
Monoclinic $a \neq b \neq c$ $\alpha \neq 90°$, $\beta = \gamma = 90°$ 	monoclinic-sphenoidal	2	C_2	3-5	1	-	-	-	-	n		
	monoclinic-domatic	m	$C_{1h} = C_s$	6-9	-	-	-	-	1	n		
	monoclinic-prismatic	$2/m$	C_{2h}	10-15	1	-	-	-	1	y		
Orthorhombic $a \neq b \neq c$ $\alpha = \beta = \gamma = 90°$ 	orthorhombic-disphenoidal	222	$V = D_2$	16-24	3	-	-	-	-	n		
	orthorhombic-pyramidal	$mm2$	C_{2v}	25-46	1	-	-	-	2	n		
											47: $YBa_2Cu_3O_{7-x}$	

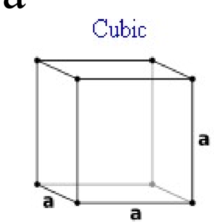
http://lamp.tu-graz.ac.at/~hadley/ss2/crystalphysics/crystalclasses/crystalclasses.html

Cubic crystals

All second rank tensors of cubic crystals reduce to constants

Electrical conductivity, thermal conductivity, electric susceptibility, magnetic susceptibility, Peltier effect (heat current due to electrical current), Seebeck effect (Electric field due to thermal gradient)

216: ZnS, GaAs, GaP, InAs, SiC
221: CsCl, cubic perovskite
225: Al, Cu, Ni, Ag, Pt, Au, Pb, NaCl
227: C, Si, Ge, spinel
229: Na, K, Cr, Fe, Nb, Mo, Ta



23	T	195-199		12
$m3$	T_h	200-206		24
432	O	207-214		24
$\bar{4}3m$	T_d	215-220	216: Zincblende, ZnS, GaAs, GaP, InAs, SiC	24
$m3m$	O_h	221-230	221: CsCl, cubic perovskite 225: fcc, Al, Cu, Ni, Ag, Pt, Au, Pb, γ-Fe, NaCl 227: diamond, C, Si,	48

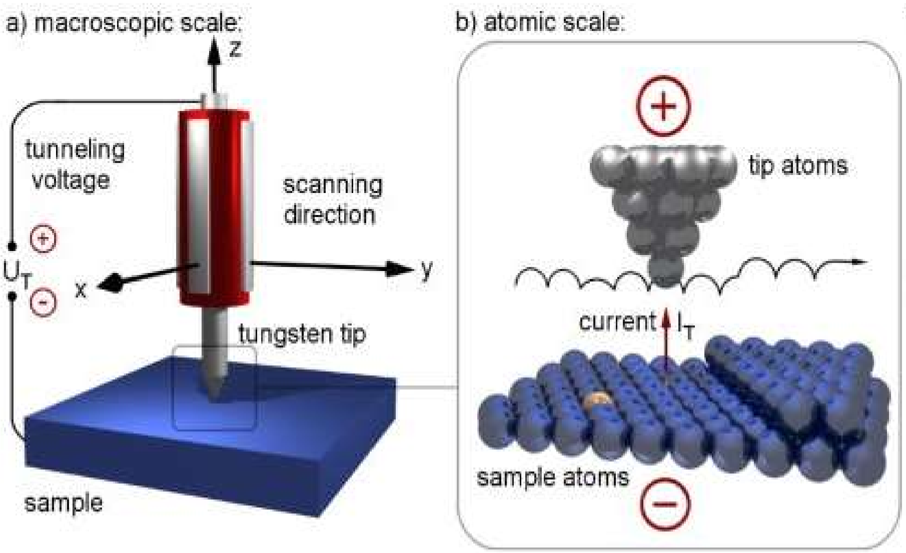
$$\begin{bmatrix} g_{11} & 0 & 0 \\ & g_{11} & 0 \\ & & g_{11} \end{bmatrix}$$

Material	ρ (Ω•m) at 20 °C	σ (S/m) at 20 °C	Temperature coefficient[note 1] (K^{-1})	Reference
Silver	1.59×10^{-8}	6.30×10^{7}	0.0038	[7][8]
Copper	1.68×10^{-8}	5.96×10^{7}	0.0039	[8]
Annealed copper[note 2]	1.72×10^{-8}	5.80×10^{7}		[citation needed]
Gold[note 3]	2.44×10^{-8}	4.10×10^{7}	0.0034	[7]
Aluminium[note 4]	2.82×10^{-8}	3.5×10^{7}	0.0039	[7]
Calcium	3.36×10^{-8}	2.98×10^{7}	0.0041	
Tungsten	5.60×10^{-8}	1.79×10^{7}	0.0045	[7]
Zinc	5.90×10^{-8}	1.69×10^{7}	0.0037	[9]
Nickel	6.99×10^{-8}	1.43×10^{7}	0.006	
Lithium	9.28×10^{-8}	1.08×10^{7}	0.006	
Iron	1.0×10^{-7}	1.00×10^{7}	0.005	[7]
Platinum	1.06×10^{-7}	9.43×10^{6}	0.00392	[7]
Tin	1.09×10^{-7}	9.17×10^{6}	0.0045	
Carbon steel (1010)	1.43×10^{-7}	6.99×10^{6}		[10]
Lead	2.2×10^{-7}	4.55×10^{6}	0.0039	[7]
Titanium	4.20×10^{-7}	2.38×10^{6}	X	
Grain oriented electrical steel	4.60×10^{-7}	2.17×10^{6}		[11]
Manganin	4.82×10^{-7}	2.07×10^{6}	0.000002	[12]
Constantan	4.9×10^{-7}	2.04×10^{6}	0.000008	[13]
Stainless steel[note 5]	6.9×10^{-7}	1.45×10^{6}		[14]
Mercury	9.8×10^{-7}	1.02×10^{6}	0.0009	[12]
Nichrome[note 6]	1.10×10^{-6}	9.09×10^{5}	0.0004	[7]
GaAs	5×10^{-7} to 10×10^{-3}	5×10^{-8} to 10^{3}		[15]
Carbon (amorphous)	5×10^{-4} to 8×10^{-4}	1.25 to 2×10^{3}	−0.0005	[7][16]
Carbon (graphite)[note 7]	2.5e$\times10^{-6}$ to 5.0×10^{-6} //basal plane 3.0×10^{-3} ⊥basal plane	2 to 3×10^{5} //basal plane 3.3×10^{2} ⊥basal plane		[17]
Carbon (diamond)[note 8]	1×10^{12}	$\sim10^{-13}$		[18]
Germanium[note 8]	4.6×10^{-1}	2.17	−0.048	[7][8]
Sea water[note 9]	2×10^{-1}	4.8		[19]
Drinking water[note 10]	2×10^{1} to 2×10^{3}	5×10^{-4} to 5×10^{-2}		[citation needed]

Piezoelectricity (rank 3 tensor)

AFM's, STM's
Quartz crystal oscillators
Surface acoustic wave generators
Pressure sensors - Epcos
Fuel injectors - Bosch
Inkjet printers

No inversion symmetry



lead zirconate titanate ($Pb[Zr_xTi_{1-x}]O_3$ $0<x<1$)
—more commonly known as PZT
barium titanate ($BaTiO_3$)
lead titanate ($PbTiO_3$)
potassium niobate ($KNbO_3$)
lithium niobate ($LiNbO_3$)
lithium tantalate ($LiTaO_3$)
sodium tungstate (Na_2WO_3)
$Ba_2NaNb_5O_5$
$Pb_2KNb_5O_{15}$

Piezoelectric crystal classes: 1, 2, m, 222, mm2, 4, -4, 422, 4mm, -42m, 3, 32, 3m, 6, -6, 622, 6mm, -62m, 23, -43m

The 32 Crystal Classes

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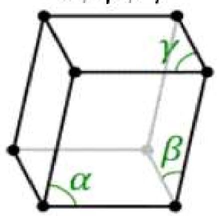
Triclinic $a \neq b \neq c$ $\alpha \neq \beta \neq \gamma$ 	triclinic-pedial	1	C_1	1	-	-	-	-	-	n		
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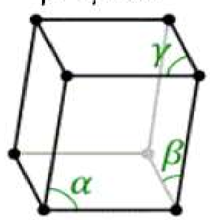
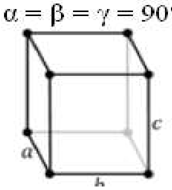
Monoclinic $a \neq b \neq c$ $\alpha \neq 90°$, $\beta = \gamma = 90°$ 	monoclinic-sphenoidal	2	C_2	3-5	1	-	-	-	-	n		
	monoclinic-domatic	m	$C_{1h} = C_s$	6-9	-	-	-	-	1	n		
	monoclinic-prismatic	$2/m$	C_{2h}	10-15	1	-	-	-	1	y		
Orthorhombic $a \neq b \neq c$ $\alpha = \beta = \gamma = 90°$ 	orthorhombic-disphenoidal	222	$V = D_2$	16-24	3	-	-	-	-	n		
	orthorhombic-pyramidal	$mm2$	C_{2v}	25-46	1	-	-	-	2	n		
											47: $YBa_2Cu_3O_{7-x}$	

http://lamp.tu-graz.ac.at/~hadley/ss2/crystalphysics/crystalclasses/crystalclasses.html

Tensor notation

We need a way to represent 3rd and 4th rank tensors in 2-d.

$$1\,1 \rightarrow 1 \quad 1\,2 \rightarrow 6 \quad 1\,3 \rightarrow 5$$

$$2\,2 \rightarrow 2 \quad 2\,3 \rightarrow 4$$

$$3\,3 \rightarrow 3$$

rank 3

$$g_{36} \rightarrow g_{312}$$

rank 4

$$g_{14} \rightarrow g_{1123}$$