Pyroelectricity

Pyroelectricity is described by a rank 1 tensor

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

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

rank 1: pyroelectric effect, pyromagnetic effect, electrocaloric effect, magnetocaloric effect

Rank 2 Tensors

Electric susceptibility
Dielectric constant
Magnetic susceptibility
Thermal expansion
Electrical conductivity
Thermal conductivity
Seebeck effect
Peltier effect

Polarization tensor

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

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

Transforming P and E by a crystal symmetry must leave the polarization 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 generating matrix,

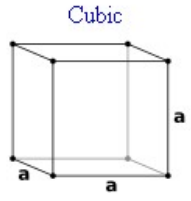
$$U = \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \qquad U^{-1} = U = \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \qquad U^{-1}\chi U = \begin{bmatrix} \chi_{xx} & \chi_{xy} & -\chi_{xz} \\ \chi_{yx} & \chi_{yy} & -\chi_{yz} \\ -\chi_{zx} & -\chi_{zy} &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

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

Cubic crystals

All second rank tensors of cubic crystals reduce to constants

216: ZnS, GaAs, GaP, InAs
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

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

Rank 3 Tensors

Piezoelectricity
Piezomagnetism
Hall effect
Nerst effect
Ettingshausen effect
Nonlinear electrical susceptibility

Nonlinear optics

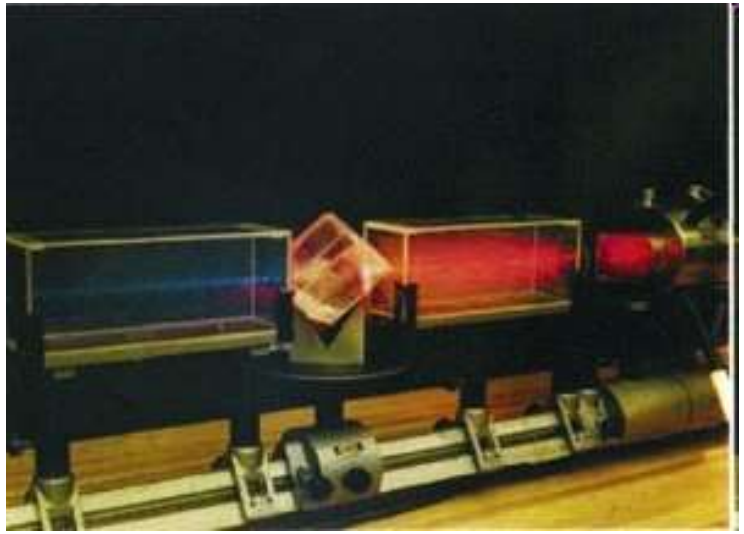
Period doubling crystals

no inversion symmetry

$$P = \chi^{(1)}E + \chi^{(2)}E^2 + \chi^{(3)}E^3 + \cdots$$

$$P_i = \frac{-\partial^2 G}{\partial E_i \partial E_j} E_j + \frac{1}{2}\frac{-\partial^3 G}{\partial E_i \partial E_j \partial E_k} E_j E_k + \cdots$$

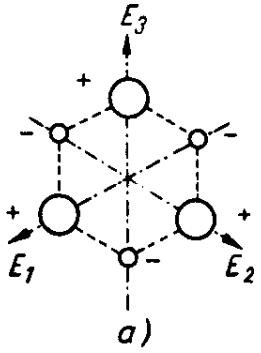
$$\cos^2(\omega t) = \tfrac{1}{2}\left(1 + \cos(2\omega t)\right)$$

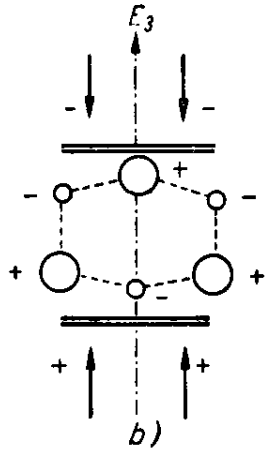


806 nm light : lithium iodate ($LiIO_3$)
860 nm light : potassium niobate ($KNbO_3$)
980 nm light : $KNbO_3$
1064 nm light : monopotassium phosphate (KH_2PO_4, KDP), lithium triborate (LBO).
1300 nm light : gallium selenide (GaSe)
1319 nm light : $KNbO_3$, BBO, KDP, lithium niobate ($LiNbO_3$), $LiIO_3$

Piezoelectricity

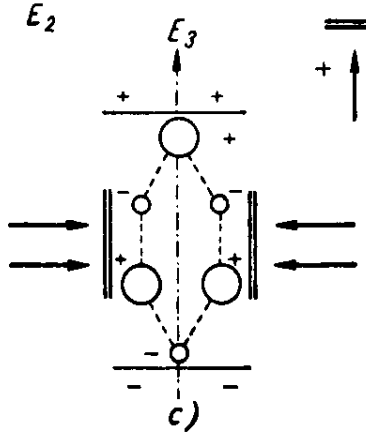
average position +
is
average position -





$$P_k = -\left(\frac{\partial G}{\partial E_k}\right)$$

average position +
not
average position -



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

Rank 4 Tensors

Stiffness tensor
Compliance tensor
Piezoconductivity
Electrostriction
Magnetostriction
How the Seebeck effect depends on stress
How the electric susceptibility depends on stress
How the magnetic susceptibility depends on stress
Nonlinear electric susceptibility
Nonlinear magnetic susceptibility

Electrostriction

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

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

piezoelectricity

Electrostriction

Rutile

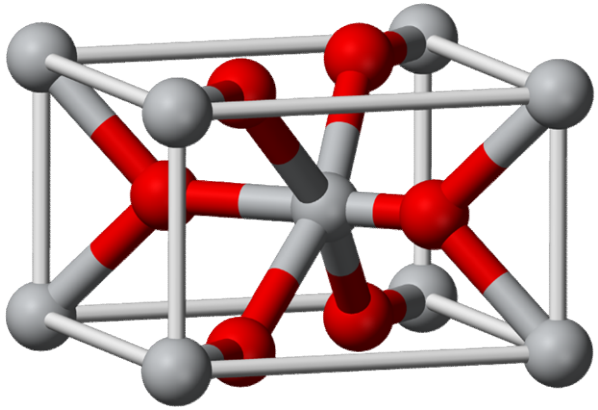

```
_symmetry_equiv_pos_as_xyz
1 '-y+1/2, x+1/2, -z+1/2'
2 'y+1/2, -x+1/2, -z+1/2'
3 'y, x, -z'
4 '-y, -x, -z'
5 'y+1/2, -x+1/2, z+1/2'
6 '-y+1/2, x+1/2, z+1/2'
7 '-y, -x, z'
8 'y, x, z'
9 'x+1/2, -y+1/2, -z+1/2'
10 '-x+1/2, y+1/2, -z+1/2'
11 'x, y, -z'
12 '-x, -y, -z'
13 '-x+1/2, y+1/2, z+1/2'
14 'x+1/2, -y+1/2, z+1/2'
15 '-x, -y, z'
16 'x, y, z'
loop_
_atom_type_symbol
_atom_type_oxidation_number
Ti4+ 4
O2- -2
loop_
_atom_site_label
_atom_site_type_symbol
_atom_site_symmetry_multiplicity
_atom_site_Wyckoff_symbol
_atom_site_fract_x
_atom_site_fract_y
_atom_site_fract_z
_atom_site_B_iso_or_equiv
_atom_site_occupancy
_atom_site_attached_hydrogens
Ti1 Ti4+ 2 a 0 0 0 . 1. 0
O1 O2- 4 f 0.30479(10) 0.30479(10) 0 . 1. 0
```

re known:

al mineral of pseudo-octahedral habit

own crystal, and also exhibits a
it is useful for the manufacture of certain
avelengths up to about 4.5μm.

d tantalum. Rutile derives its name from
mens when viewed by transmitted light.



ı high-temperature and high-pressure
s.

able polymorph of TiO_2 at all
energy than metastable phases of
e transformation of the metastable TiO

Rutile

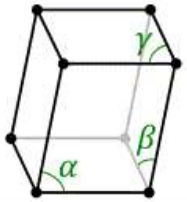
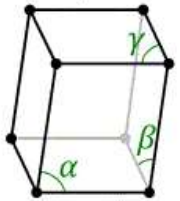
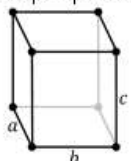
Wine-red rutile crystals from Binn Valley in Switzerland (Size: 2.0 x 1.6 x 0.8 cm)

General

Category	Oxide minerals
Formula (repeating unit)	TiO_2
Strunz classification	04.DB.05
Crystal symmetry	Tetragonal ditetragonal dipyramidal H-M symbol: (4/m 2/m 2/m) Space group: P 4/mnm
Unit cell	a = 4.5937 Å, c = 2.9587 Å; Z = 2

Identification

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	Number of symmetry elements
Triclinic $a \neq b \neq c$ $\alpha \neq \beta \neq \gamma$ 	triclinic-pedial	1	C_1	1	-	-	-	-	-	n		1
	triclinic-pinacoidal	$\bar{1}$	$S_2 = C_i$	2	-	-	-	-	-	y		2
Monoclinic $a \neq b \neq c$ $\alpha \neq 90°$, $\beta = \gamma = 90°$ 	monoclinic-sphenoidal	2	C_2	3-5	1	-	-	-	-	n		2
	monoclinic-domatic	m	$C_{1h} = C_s$	6-9	-	-	-	-	1	n		2
	monoclinic-prismatic	$2/m$	C_{2h}	10-15	1	-	-	-	1	y		4
Orthorhombic $a \neq b \neq c$ $\alpha = \beta = \gamma = 90°$ 	orthorhombic-disphenoidal	222	$V = D_2$	16-24	3	-	-	-	-	n		4
	orthorhombic-pyramidal	$mm2$	C_{2v}	25-46	1	-	-	-	2	n		4
											47: $YBa_2Cu_3O_{7-x}$	

International Tables for Crystallography
Volume A: Space-group symmetry

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Edited by Th. Hahn

| **contents** | indexes |

| contributors | editors |

| sample pages | purchase |

| explanation of the space-group data |

Go to space group **No.** 1 (P 1) Go

| symmetry database |

Volume A treats crystallographic symmetry in direct or physical space. It contains extensive tabulations and illustrations of the 17 plane grou crystallographic point groups.

The first five parts of the volume contain introductory material: lists of symbols and terms; a guide to the use of the space-group tables; the c space-group symbols; and unit-cell (coordinate) transformations. These are followed by the plane-group and space-group tables (Parts 6 and information is presented:

- headline with the relevant group symbols;
- diagrams of the symmetry elements and of the general position;
- specification of the origin and the asymmetric unit;
- list of symmetry operations;

Symmetric and asymmetric tensors

$$-\left(\frac{\partial^2 G}{\partial E_j \partial E_k}\right) = \frac{\partial P_k}{\partial E_j} = \chi_{kj} = -\left(\frac{\partial^2 G}{\partial E_k \partial E_j}\right) = \frac{\partial P_j}{\partial E_k} = \chi_{jk}$$

Symmetric

- electric susceptibility
- magnetic susceptibility
- electrical conductivity
- thermal conductivity
- stiffness tensor

Asymmetric

- Seebeck effect
- Peltier effect
- piezoconductivity

Structural phase transitions

Some materials make a transition from one crystal structure to another.

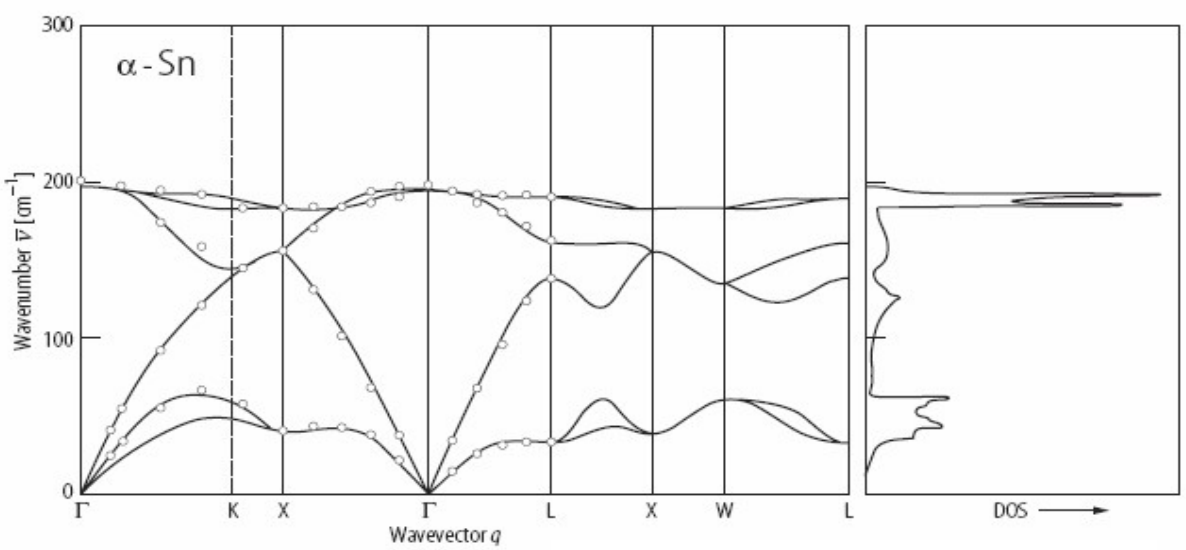
Two allotropes of tin: gray tin (α-Sn) is stable at temperatures below 13.2°C and white tin (β-Sn) is stable above.

The phase with the lowest free energy prevails. (White tin can be stabilized below 13.2 C by adding impurities.)

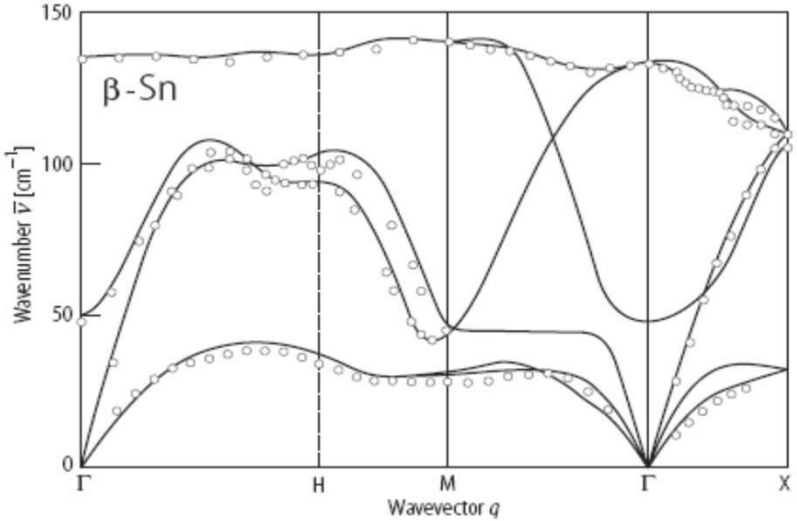
$$F = U - TS$$

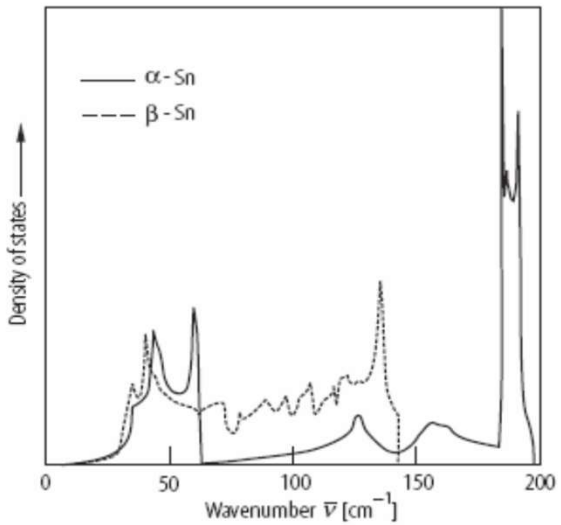
Structural phase transition in Sn

semiconductor
diamond crystal structure

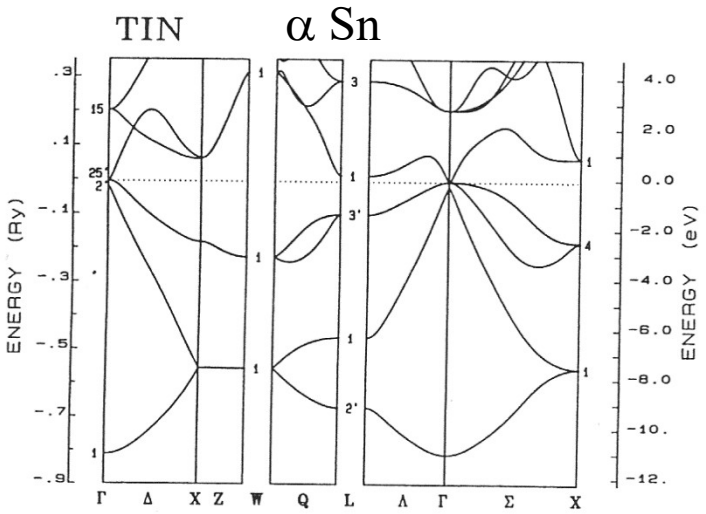


metal
tetragonal crystal structure

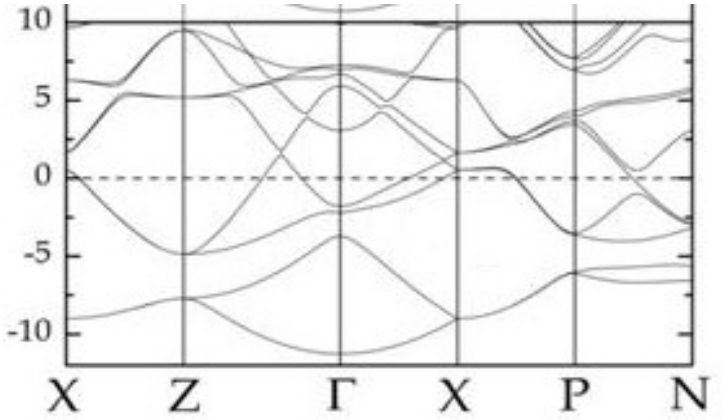




Structural phase transition in Sn



metal β Sn



$$s \approx \frac{\pi^2 D(E_F)}{3} k_B^2 T$$

semiconductor: electrons make a negligible contribution to the entropy

$$s = \frac{\sqrt{2\pi}}{2\pi^2\hbar^3}\left(m_e^* m_h^*\right)^{3/4} \exp\left(\frac{-E_g}{2k_B T}\right)\left(k_B T\right)^{3/2}\left(5k_B + \frac{E_g}{T}\right),$$