

Nonlinear Optics (WiSe 2019/20)

Lecture 2: October 25, 2019

2 Nonlinear optical susceptibilities

2.4 Properties of the nonlinear susceptibilities

2.4.1 Physical fields are real

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2.4.3 Symmetry for lossless media

2.4.4 Kleinman's symmetry

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2.4 Properties of the nonlinear susceptibilities

2.4.1 Physical fields are real

$$\chi_{ij\dots s}^{(n)}(\omega_b; \omega_1, \dots, \omega_n)^* = \chi_{ij\dots s}^{(n)}(-\omega_b; -\omega_1, \dots, -\omega_n) \quad (2.40)$$

$$\omega_b = \sum_{i=1}^n \omega_i \quad (2.41)$$

2.4.2 Permutation symmetry

numbering 1 to n arbitrary \rightarrow use symmetric definition

$$\chi_{i\dots j\dots o\dots s}^{(n)}(\omega_b; \dots \omega_l, \dots \omega_k, \dots, \omega_n) = \chi_{i\dots o\dots j\dots s}^{(n)}(\omega_b; \dots \omega_k, \dots \omega_l, \dots, \omega_n). \quad (2.42)$$

2.4.3 Symmetry for lossless media

two additional symmetries:

- imaginary part of the susceptibility describes loss and gain
→ **susceptibilities of lossless media are real**
- complete permutation symmetry independent, if the frequency is an input or output frequency

$$\chi_{i...j...o...s}^{(n)}(\omega_b; \dots \omega_l, \dots \omega_k, \dots, \omega_n) = \chi_{j...i...o...s}^{(n)}(-\omega_l; \dots -\omega_b, \dots \omega_k, \dots, \omega_n), \quad (2.43)$$

In combination with first symmetry (Eq. (2.40))

$$\chi_{i...j...o...s}^{(n)}(\omega_b; \dots \omega_l, \dots \omega_k, \dots, \omega_n) = \chi_{j...i...o...s}^{(n)}(\omega_l; \dots \omega_b, \dots -\omega_k, \dots, -\omega_n). \quad (2.44)$$

This implies that in the lossless case, the susceptibilities for sum- and difference-frequency generation are equal if the frequencies and polarizations involved are chosen accordingly. For the classical model treated before, this is immediately clear. Furthermore, it can also generally be proven by a quantum mechanical derivation of the susceptibility or with the help of the energy conservation [3].

2.4.4 Kleinman's symmetry

low-frequency range: medium lossless,
susceptibilities essentially **independent of wavelength**
→ indices of susceptibilities can arbitrarily be permuted,
nonlinearity responds instantaneously to the electric field

$$\begin{aligned}\chi_{i...j...o...s}^{(n)}(\omega_b; \dots \omega_l, \dots \omega_k, \dots, \omega_n) &= \chi_{j...i...o...s}^{(n)}(\omega_b; \dots \omega_l, \dots \omega_k, \dots, \omega_n) \quad (2.45) \\ &= \chi_{j...i...o...s}^{(n)} = \text{const.}\end{aligned}$$

$$P_i^{(2)}(t) = \sum_{jk} \chi_{ijk}^{(2)} E_j(t) E_k(t). \quad (2.46)$$

2.4.5 Neumann's principle

coordinate transformations (inversion, mirror image and rotation) \mathbf{T} of field and polarization vectors \mathbf{E} and \mathbf{P}

$$\begin{pmatrix} E'_x \\ E'_y \\ E'_z \end{pmatrix} = \begin{pmatrix} T_{x'x} & T_{x'y} & T_{x'z} \\ T_{y'x} & T_{y'y} & T_{y'z} \\ T_{z'x} & T_{z'y} & T_{z'z} \end{pmatrix} \begin{pmatrix} E_x \\ E_y \\ E_z \end{pmatrix} \quad (2.47)$$

$$\mathbf{E}' = \mathbf{T} \cdot \mathbf{E} \quad (2.48)$$

$$\mathbf{E} = \mathbf{T}^{-1} \cdot \mathbf{E}' \quad (2.49)$$

inversion, mirror image and rotation are orthogonal transformations: $\mathbf{T}^T = \mathbf{T}^{-1}$

$$\mathbf{E} = \mathbf{T}^T \cdot \mathbf{E}' \quad (2.50)$$

employing Einstein's summation convention

$$E_i = (T_{ii'})^T E_{i'} = T_{i'i} E_{i'} \quad (2.51)$$

$$P_i = T_{i'i} P_{i'} \quad (2.52)$$

relations in the two coordinate systems

$$P_i^{(n)} = \varepsilon_0 \chi_{ij\dots s}^{(n)} E_j \cdots E_s, \quad (2.53)$$

$$P_{i'}^{(n)} = \varepsilon_0 \chi_{i'j'\dots s'}^{(n)} E_{j'} \cdots E_{s'}, \quad (2.54)$$

Then

$$T_{i'i} P_i^{(n)} = P_{i'}^{(n)} = \varepsilon_0 T_{i'i} \chi_{ij\dots s}^{(n)} T_{j'j} E_{j'} T_{k'k} E_{k'} \cdots T_{s's} E_{s'} \quad (2.55)$$

$$\chi_{i'j'\dots s'}^{(n)} = T_{i'i} T_{j'j} \cdots T_{s's} \chi_{ij\dots s}^{(n)} \quad (2.56)$$

→ **nonlinear susceptibilities are tensors**

transformations, that do not change the physical reference between the fields and media, leave the susceptibilities invariant.

The **32 crystal classes**, that can be derived from the **7 crystal systems**, are characterized by being **invariant under a point group**. I.e., the susceptibility tensor of materials, belonging to a certain crystal class, must be invariant under the corresponding point group (**Neumann's principle**).

Example: let's consider inversion $T_{i'i} = (-1)\delta_{i'i}$

susceptibility tensor of the inverted medium

$$\chi_{i'j'...s'}^{(n)} = (-1)^{n+1} \chi_{ij...s}^{(n)} \quad (2.57)$$

If the medium is invariant under inversion, it follows for $n=\text{even}$

$$\chi_{ij...s}^{(n)} = (-1)^{n+1} \chi_{ij...s}^{(n)} = 0 \quad (2.58)$$

i.e., in an inversion symmetric medium, the susceptibility tensors of even orders vanish

(no linear electro-optic effect, no SHG)

Of the 32 crystal classes, already 11 possess inversion symmetry. Remaining 21 non-centrosymmetric crystal classes, the number of nonvanishing tensor elements $\chi_{ijk}^{(2)}$ further reduce because of other symmetries. The symmetry properties of $\chi_{ijk}^{(2)}$ are the same as those of the piezo-electric tensor.

If the even nonlinear optical processes are forbidden by symmetry (e.g., in media such as glasses, gases, fluids), processes of third order are the dominating nonlinearity. The existing inversion symmetry also reduces the non-vanishing susceptibility tensor elements of third order $\chi_{ijkl}^{(3)}$.

2.5 The reduced susceptibility tensor of second order

second-order susceptibilities are expressed in terms of nonlinear coefficients

$$d_{ijk} = \frac{1}{2}\chi_{ijk}^{(2)}$$

$$\hat{P}_i^{(2)}(\omega_n + \omega_m) = 2\varepsilon_0 \sum_{jk} d_{ijk}(\omega_n + \omega_m : \omega_n, \omega_m) \hat{E}_j(\omega_n) \hat{E}_k(\omega_m). \quad (2.59)$$

If Kleinmann symmetry condition is valid (or for SHG), the nonlinear coefficients can be formulated in reduced form $d_{ijk} = d_{ikj} = d_{il}$, i.e., in these cases the indices j and k can be permuted.

$$[jk] = \begin{bmatrix} 11 & 12 & 13 \\ 21 & 22 & 23 \\ 31 & 32 & 33 \end{bmatrix} = [l] = \begin{bmatrix} 1 & 6 & 5 \\ 6 & 2 & 4 \\ 5 & 4 & 3 \end{bmatrix}. \quad (2.60)$$

For SHG

$$\begin{bmatrix} P_x(2\omega) \\ P_y(2\omega) \\ P_z(2\omega) \end{bmatrix} = \varepsilon_0 \begin{bmatrix} d_{11} & d_{12} & d_{13} & d_{14} & d_{15} & d_{16} \\ d_{21} & d_{22} & d_{23} & d_{24} & d_{25} & d_{26} \\ d_{31} & d_{32} & d_{33} & d_{34} & d_{35} & d_{36} \end{bmatrix} \cdot \begin{bmatrix} E_x(\omega)^2 \\ E_y(\omega)^2 \\ E_z(\omega)^2 \\ 2E_y(\omega)E_z(\omega) \\ 2E_x(\omega)E_z(\omega) \\ 2E_x(\omega)E_y(\omega) \end{bmatrix}. \quad (2.61)$$

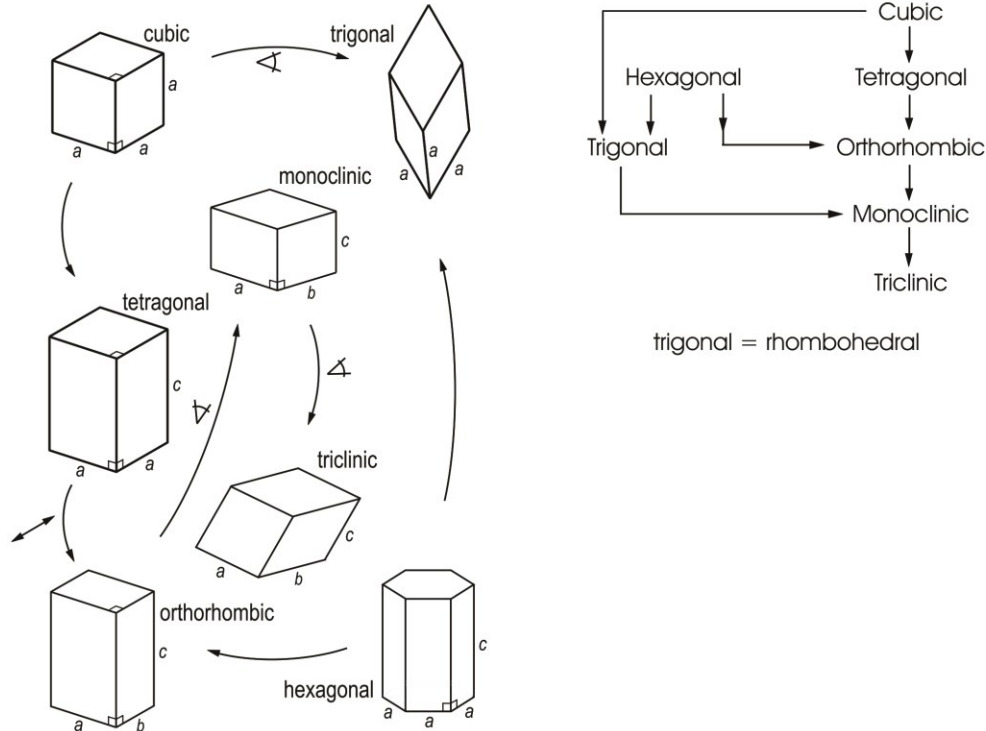
The Bravais lattices can be divided into

7 crystal systems and 14 Bravais lattices

↑
7 point groups

↑
14 space groups

The 7 crystal systems and their hierarchy:



The 14 Bravais lattices: introduction of special bases preserves the point symmetry →

3 cubic lattices:

2 tetragonal lattices:

4 orthorhombic lattices:

2 monoclinic lattices:

1 triclinic lattice

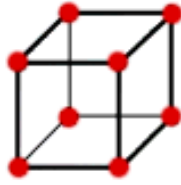
1 trigonal lattice

1 hexagonal lattice

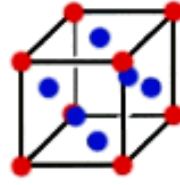
body face
sc, bcc, fcc
st, ct
so, bco, fco, bco
sm, cm
base

14 Bravais lattices in 7 crystal systems

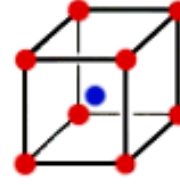
The 14 Bravais lattices



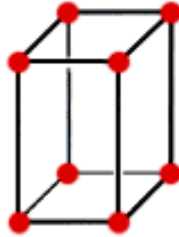
**Simple
cubic**



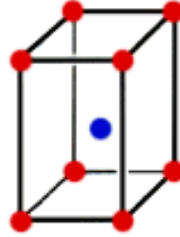
**Face-centered
cubic**



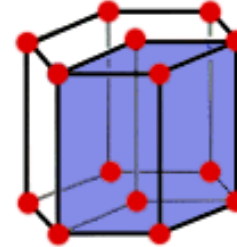
**Body-centered
cubic**



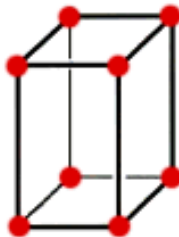
**Simple
tetragonal**



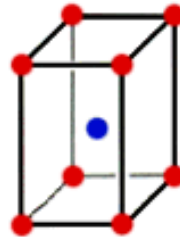
**Body-centered
tetragonal**



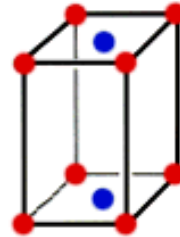
Hexagonal



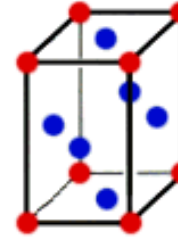
**Simple
orthorhombic**



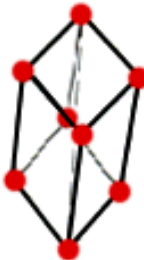
**Body-centered
orthorhombic**



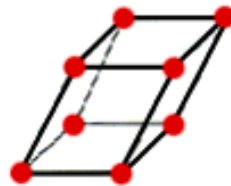
**Base-centered
orthorhombic**



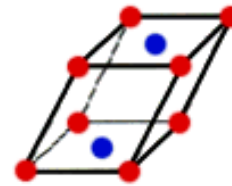
**Face-centered
orthorhombic**



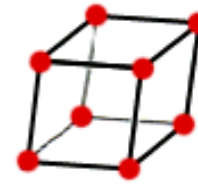
Rhombohedral



**Simple
Monoclinic**



**Base-centered
monoclinic**






























Triclinic

The crystals can be divided into

32 crystallographic point groups and 230 space groups

The 32 crystallographic point groups originate from the point groups of the 7 crystal systems by systematic reduction of the symmetry (see Ashcroft&Mermin: *Solid State Physics*, Chapter 7, Tables 7.2 and 7.3, Saunders College Publ. (1976):

Schoenflies	Hexagonal	Tetragonal	Trigonal	Orthorhombic	Monoclinic	Triclinic	International
C_n	C_6  6	C_4  4	C_3  3		C_2  2	C_1  1	n
C_{nv}	C_{6v}  6mm	C_{4v}  4mm	C_{3v}  3m	C_{2v}  2mm			nmm (n even) nm (n odd)
C_{nh}	C_{6h}  6/m	C_{4h}  4/m		C_{2h}  2/m			n/m
	C_{3h}  $\bar{6}$			C_{1h} ($\bar{2}$)  m			\bar{n}
S_n		S_4  $\bar{4}$	S_6  (C_{3i}) $\bar{3}$		S_2  (C_i) $\bar{1}$		
D_n	D_6  622	D_4  422	D_3  32	D_2  (V) 222			$n22$ (n even) $n2$ (n odd)
D_{nh}	D_{6h}  6/mmm	D_{4h}  4/mmm		D_{2h} (mmm)  (V_h) 2/mmm			$\frac{n}{2} \frac{2}{m} \frac{2}{m}$ (n/mmm)
	D_{3h}  $\bar{6}2m$						$\bar{n}2m$ (n even)
D_{nd}		D_{2d}  (V_d) $\bar{4}2m$	D_{3d} ($\bar{3}m$)  $\bar{3}2$				$\bar{n} \frac{2}{m}$ (n odd)

noncubic

7

7

5

3

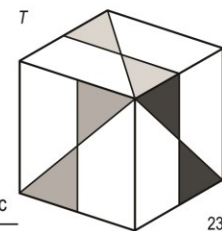
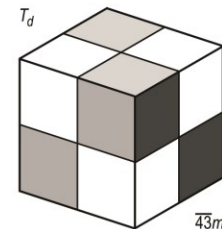
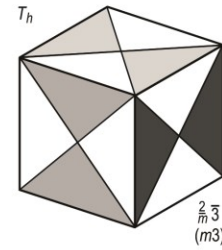
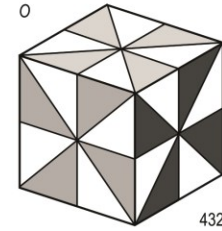
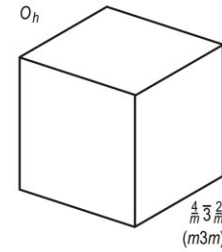
3

2

⇒ 32 point groups

5

Cubic



$\bar{3}2$

crystal system	crystal class	(d_{il})	
triclinic	$C_1 \parallel 1$	$\begin{pmatrix} d_{11} & d_{12} & d_{13} & d_{14} & d_{15} & d_{16} \\ d_{21} & d_{22} & d_{23} & d_{24} & d_{25} & d_{26} \\ d_{31} & d_{32} & d_{33} & d_{34} & d_{35} & d_{36} \end{pmatrix}$	
monoclinic	$C_S \parallel m$	$\begin{pmatrix} d_{11} & d_{12} & d_{13} & 0 & 0 & d_{16} \\ d_{21} & d_{22} & d_{23} & 0 & 0 & d_{26} \\ 0 & 0 & 0 & d_{34} & d_{35} & 0 \end{pmatrix}$	$m \perp z$
	$C_S \parallel m$	$\begin{pmatrix} d_{11} & d_{12} & d_{13} & 0 & d_{15} & 0 \\ 0 & 0 & 0 & d_{24} & 0 & d_{26} \\ d_{31} & d_{32} & d_{33} & 0 & d_{35} & 0 \end{pmatrix}$	$m \perp y$ IRE conv.
	$C_2 \parallel 2$	$\begin{pmatrix} 0 & 0 & 0 & d_{14} & d_{15} & 0 \\ 0 & 0 & 0 & d_{24} & d_{25} & 0 \\ d_{31} & d_{32} & d_{33} & 0 & 0 & d_{36} \end{pmatrix}$	$2 \perp z$
	$C_2 \parallel 2$	$\begin{pmatrix} 0 & 0 & 0 & d_{14} & 0 & d_{16} \\ d_{21} & d_{22} & d_{23} & 0 & d_{25} & 0 \\ 0 & 0 & 0 & d_{34} & 0 & d_{36} \end{pmatrix}$	$2 \perp y$ IRE conv.
ortho- rhombic	$C_{2v} \parallel mm2$	$\begin{pmatrix} 0 & 0 & 0 & 0 & d_{15} & 0 \\ 0 & 0 & 0 & d_{24} & 0 & 0 \\ d_{31} & d_{32} & d_{33} & 0 & 0 & 0 \end{pmatrix}$	KTP, KNbO ₃ BaNaNb ₅ O ₁₅ LiB ₃ O ₃ (LBO)
	$D_2 \parallel 222$	$\begin{pmatrix} 0 & 0 & 0 & d_{14} & 0 & 0 \\ 0 & 0 & 0 & 0 & d_{25} & 0 \\ 0 & 0 & 0 & 0 & 0 & d_{36} \end{pmatrix}$	α -HIO ₃

crystal system	crystal class	(d_{il})					
tetra- gonal	$C_4 \parallel 4$	$\begin{pmatrix} 0 & 0 & 0 & d_{14} & d_{15} & 0 \\ 0 & 0 & 0 & d_{15} & -d_{14} & 0 \\ d_{31} & d_{31} & d_{33} & 0 & 0 & 0 \end{pmatrix}$					
	$S_4 \parallel \bar{4}$	$\begin{pmatrix} 0 & 0 & 0 & d_{14} & d_{15} & 0 \\ 0 & 0 & 0 & -d_{15} & d_{14} & 0 \\ d_{31} & -d_{31} & 0 & 0 & 0 & d_{36} \end{pmatrix}$					
	$C_{4v} \parallel 4mm$	$\begin{pmatrix} 0 & 0 & 0 & 0 & d_{15} & 0 \\ 0 & 0 & 0 & d_{15} & 0 & 0 \\ d_{31} & d_{31} & d_{33} & 0 & 0 & 0 \end{pmatrix}$					
	$D_{2d} \parallel \bar{4}2m$	$\begin{pmatrix} 0 & 0 & 0 & d_{14} & 0 & 0 \\ 0 & 0 & 0 & 0 & d_{14} & 0 \\ 0 & 0 & 0 & 0 & 0 & d_{36} \end{pmatrix}$					
							NH ₄ H ₂ PO ₄ (ADP) KH ₂ PO ₄ (KDP) CsH ₂ AsO ₄ (CDA) AgGaSe
	$D_4 \parallel 422$	$\begin{pmatrix} 0 & 0 & 0 & d_{14} & 0 & 0 \\ 0 & 0 & 0 & 0 & -d_{14} & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \end{pmatrix}$					
trigonal	$C_3 \parallel 3$	$\begin{pmatrix} d_{11} & -d_{11} & 0 & d_{14} & d_{15} & -d_{22} \\ -d_{22} & d_{22} & 0 & d_{15} & -d_{14} & -d_{11} \\ d_{31} & d_{31} & d_{33} & 0 & 0 & 0 \end{pmatrix}$					
	$C_{3v} \parallel 3m$	$\begin{pmatrix} 0 & 0 & 0 & 0 & d_{15} & -d_{22} \\ -d_{22} & d_{22} & 0 & d_{15} & 0 & 0 \\ d_{31} & d_{31} & d_{33} & 0 & 0 & 0 \end{pmatrix}$					
							$m \perp x$ IRE conv. LiNbO ₃ , LiTaO ₂ BaB ₂ O ₂ (BBO)
	$C_{3v} \parallel 3m$	$\begin{pmatrix} d_{11} & -d_{11} & 0 & 0 & d_{15} & 0 \\ 0 & 0 & 0 & d_{15} & 0 & -d_{11} \\ d_{31} & d_{31} & d_{33} & 0 & 0 & 0 \end{pmatrix}$					
							$m \perp y$
	$D_3 \parallel 32$	$\begin{pmatrix} d_{11} & -d_{11} & 0 & d_{14} & 0 & 0 \\ 0 & 0 & 0 & 0 & -d_{14} & -d_{11} \\ 0 & 0 & 0 & 0 & 0 & 0 \end{pmatrix}$					
							SiO ₂ , Te

crystal system	crystal class	(d_{il})	
hexa- gonal	$C_{3k} \parallel \bar{6}$	$\begin{pmatrix} d_{11} & -d_{11} & 0 & 0 & 0 & -d_{22} \\ -d_{22} & d_{22} & 0 & 0 & 0 & -d_{11} \\ 0 & 0 & 0 & 0 & 0 & 0 \end{pmatrix}$	
	$C_{3k} \parallel 6$	$\begin{pmatrix} 0 & 0 & 0 & d_{14} & d_{15} & 0 \\ 0 & 0 & 0 & d_{15} & -d_{14} & 0 \\ d_{31} & d_{32} & d_{33} & 0 & 0 & 0 \end{pmatrix}$	LiIO ₃
		like class $C_4 \parallel 4$	
	$D_{3k} \parallel \bar{6}m2$	$\begin{pmatrix} 0 & 0 & 0 & 0 & 0 & -d_{22} \\ -d_{22} & d_{22} & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \end{pmatrix}$	$m \perp x$ IRE conv.
	$D_{3k} \parallel \bar{6}m2$	$\begin{pmatrix} d_{11} & -d_{11} & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & -d_{11} \\ 0 & 0 & 0 & 0 & 0 & 0 \end{pmatrix}$	$m \perp y$
cubic	$C_{6\nu} \parallel 6mm$	$\begin{pmatrix} 0 & 0 & 0 & 0 & d_{15} & 0 \\ 0 & 0 & 0 & d_{15} & 0 & 0 \\ d_{31} & d_{31} & d_{33} & 0 & 0 & 0 \end{pmatrix}$	CdS, CdSe ZnO, ZnS
		like class $C_{4\nu} \parallel 4mm$	
	$D_6 \parallel 622$	$\begin{pmatrix} 0 & 0 & 0 & d_{14} & 0 & 0 \\ 0 & 0 & 0 & 0 & -d_{14} & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \end{pmatrix}$	
		like class $D_4 \parallel 422$	
	$T \parallel 23$	$\begin{pmatrix} 0 & 0 & 0 & d_{14} & 0 & 0 \\ 0 & 0 & 0 & 0 & d_{14} & 0 \\ 0 & 0 & 0 & 0 & 0 & d_{14} \end{pmatrix}$	
	$T_d \parallel \bar{4}3m$	$\begin{pmatrix} 0 & 0 & 0 & d_{14} & 0 & 0 \\ 0 & 0 & 0 & 0 & d_{14} & 0 \\ 0 & 0 & 0 & 0 & 0 & d_{14} \end{pmatrix}$	GaAs, InP InSb
	$O \parallel 432$	all elements vanish	

crystal	$d_{ij}^{(2)} (2\omega : \omega, \omega) [10^{-12} \frac{m}{V}]$	$\delta_{ijk} [10^{-13} \frac{V}{m}]$
Te	$d_{11} = +690$ (@ $\lambda = 10.6 \mu\text{m}$)	+0.7
CdGeAs ₂	$d_{36} = +264$ (@ $\lambda = 10.6 \mu\text{m}$)	+1.72
InP	$d_{14} = +263$	+1.3
GaAs	$d_{14} = +105$ (@ $\lambda = 10.6 \mu\text{m}$)	+1.15
KNbO ₃	$d_{33} = -20.3$	-4.43
	$d_{31} = -11.3$	-2.04
	$d_{32} = -13.5$	-2.12
LiNbO ₃	$d_{31} = -4$	-.62
	$d_{33} = -27$	-3.9
BaTiO ₃	$d_{33} = -5$	-0.7
	$d_{31} = -13.5$	-1.91
Ba ₂ NaNb ₅ O ₁₅	$d_{33} = -21$	+3.72
	$d_{32} = -15$	+2.21
LiIO ₃	$d_{31} = -4.4$	+3.45
KH ₂ PO ₄ (KDP)	$d_{36} = d_{14} = +0.39$	+2.3
NH ₄ H ₂ PO ₄ (ADP)	$d_{36} = d_{14} = +0.47$	+2.5
SiO ₂ (Quartz)	$d_{11} = +0.3$	+1.15
KTiPO ₄ (KTP)	$d_{31} = d_{32} = +3.3$	+2.3
β -BaB ₂ O ₄ (BBO)	$d_{22} = +2.3$	+4.16
	$d_{31} = +0.1$	+0.177
LiB ₃ O ₅ (LBO)	$d_{31} = +1.1$	+2.124
	$d_{32} = -1.0$	+1.95
DAST	$d_{11} = 630$ (@ $\lambda = 1.5 \mu\text{m}$)	+65.5

Table 2.1: Nonlinear optical coefficients for frequency doubling and Miller coefficients of several important anorganic materials and the organic material DAST.

Example to illustrate how the susceptibility tensor of a crystal class, that is invariant with respect to a point group, is restricted:

point group mm2 (e.g., KTP und KNbPO₄)

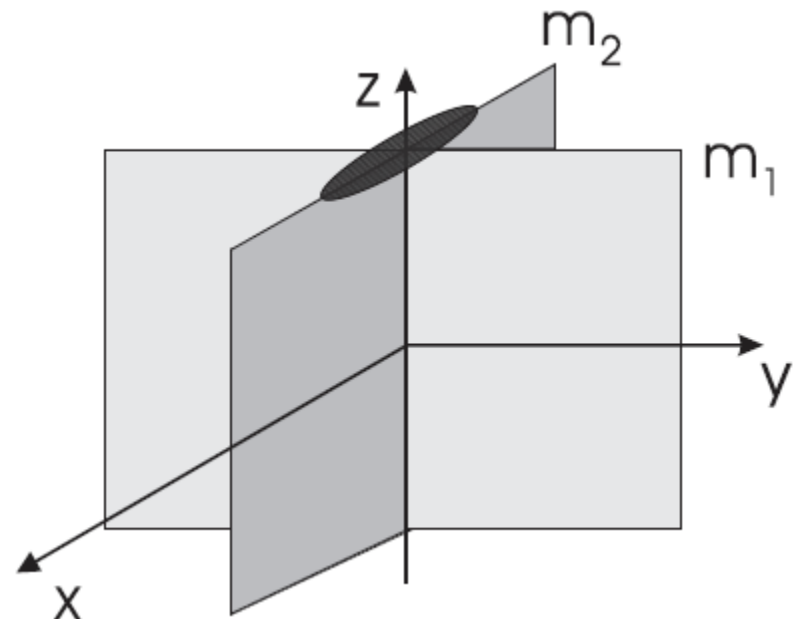
This crystal class is invariant under 180° rotations around z-axis and mirror images on the planes m₁ and m₂, that contain the rotation axis

tensor elements transform just like the coordinates

$$m_1 : (x, y, z) \longrightarrow (-x, y, z),$$

$$m_2 : (x, y, z) \longrightarrow (x, -y, z),$$

$$2 : (x, y, z) \longrightarrow (-x, -y, z)$$



From the two mirror images follows that all elements of the d tensor, for which an odd number of occurrence of the index 1 or 2 happens, must vanish,

$$\begin{aligned} d_{1,1,1} &= d_{1,2,2} = d_{1,3,3} = d_{1,2,3} = 0 \\ d_{2,1,1} &= d_{2,2,2} = d_{2,3,3} = d_{2,1,3} = 0 \\ d_{3,1,3} &= d_{3,2,3} = d_{3,1,2} = 0. \end{aligned}$$

The 2-fold axis requires, that the tensor elements, for which the indices 1 and 2 together occur an odd number of times, must vanish

$$\begin{aligned} d_{1,1,2} &= 0, & d_{1,1,3} &\neq 0 \\ d_{2,2,1} &= 0, & d_{2,2,3} &\neq 0 \\ d_{3,1,1} &\neq 0, & d_{3,2,2} &\neq 0, & d_{3,3,3} &\neq 0 \end{aligned}$$

For the point group mm2 then the following relation between nonlinear polarization and field holds

$$\begin{aligned} \hat{P}_x(2\omega; \omega, \omega) &= 2\varepsilon_0 d_{15} \hat{E}_x(\omega) \hat{E}_z(\omega) \\ \hat{P}_y(2\omega; \omega, \omega) &= 2\varepsilon_0 d_{24} \hat{E}_y(\omega) \hat{E}_z(\omega) \\ \hat{P}_z(2\omega; \omega, \omega) &= \varepsilon_0 d_{31} \hat{E}_x^2(\omega) + \varepsilon_0 d_{32} \hat{E}_y^2(\omega) + \varepsilon_0 d_{33} \hat{E}_z^2(\omega) \end{aligned}$$

2.6 The third-order susceptibility tensor

If the second-order nonlinear processes are forbidden by symmetry, then the dominating nonlinearities are of third order.

This is obviously the case in particular for isotropic media, such as liquids, gases or glasses, as they are inversion symmetric.

Isotropic media in addition possess other symmetry properties, e.g., invariance under mirror imaging on a plane. This symmetry requires that **each index must occur twice**, unless the corresponding tensor element vanishes.

→ the **possible $3^4=81$ tensor elements** already **reduce to 21 elements**.

The cubic symmetry, i.e., symmetry with respect to 90° rotations around one of the axes, in addition requires, that the number of independent tensor elements are reduced to 3 (compare exercise):

$$\begin{aligned}
xyxy &= yyxx = xxzz = zzxx = yyzz = zzyy \\
xyxy &= yxyx = xzxz = zxzx = yzyz = zyzy \\
xyyx &= yxxy = xzzx = zxzx = yzzz = zyyz \\
xxxx &= yyyy = zzzz = (xyxy + xyxy + xyyx)
\end{aligned}$$

The nonvanishing tensor elements for the various crystal classes are summarized in the table below [4], where the following notation for tensor elements is employed:

$$\hat{P}_i(3\omega; \omega, \omega, \omega) = \varepsilon_0 c_{ijkl} \hat{E}_j(\omega) \hat{E}_k(\omega) \hat{E}_l(\omega).$$

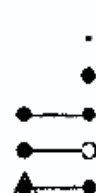
The last three indices are again permutable, for this reason a reduced notation is used

$$c_{ijkl} = c_{ip}$$

for the last three indices according to the following list:

p	1	2	3	4	5	6	7	8	9	0
jkl	111	222	333	233	133	223	113	122	112	123

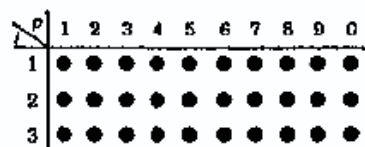
Notation:



$c_{ip} = 0$
 $c_{ip} \neq 0$
 $c_{ip} = c'_{ip}$
 $c_{ip} = -c'_{ip}$
 $c_{ip} = 3c'_{ip}$

Triklin

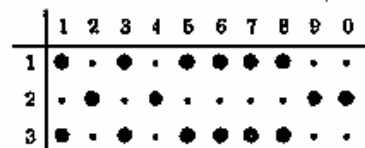
$1, \bar{1}$



Monoklin

$2, m, 2/m$

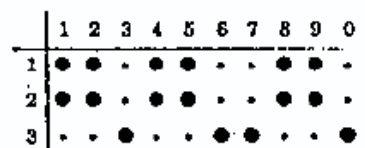
$2//x_2, m \perp x_2$



Monoklin

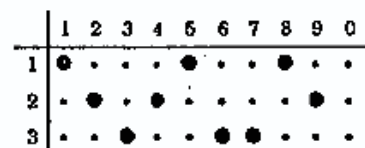
$2, m, 2/m$

$2//x_3, m \perp x_3$



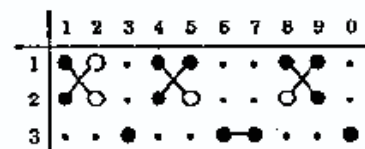
Orthorhombisch

$222, mm2, mmm$



Tetragonal

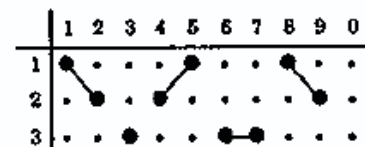
$4, \bar{4}, 4/m$



Tetragonal

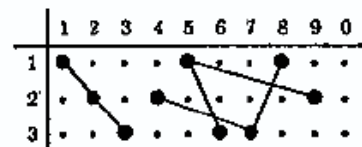
$422, 4mm$

$\bar{4}2m, 4mmm$



Kubisch

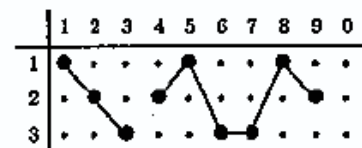
$23, m\bar{3}$



Kubisch

$432, \bar{4}3m$

$m\bar{3}m$



Trigonal

$3, \bar{3}$



Trigonal

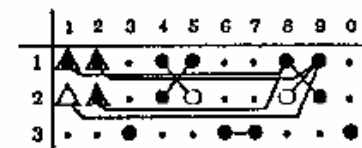
$32, 3m, \bar{3}m$



Hexagonal

$6, \bar{6}, 6/m$

$\infty, \infty/m$



Hexagonal

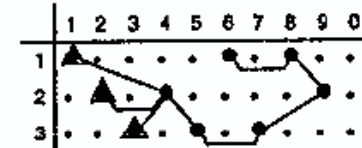
$622, 6mm, \bar{6}m2,$

$6/mmm, \infty2, \infty m,$

$\infty/m m$



$\infty, \infty, \infty \infty m$



Chapter 3: The wave equation with sources

The polarization is a source for electromagnetic fields. From Maxwell's equations we have (in SI units)

$$\begin{aligned}\nabla \times \mathbf{E} &= -\frac{\partial \mathbf{B}}{\partial t}, & (\text{Faraday}) \\ \nabla \times \mathbf{H} &= \mathbf{J} + \frac{\partial \mathbf{D}}{\partial t}. & (\text{Ampère, Maxwell})\end{aligned}$$

The material equations for a non-magnetic medium are

$$\begin{aligned}\mathbf{B} &= \mu_0 \mathbf{H}, \\ \mathbf{D} &= \varepsilon_0 \mathbf{E} + \mathbf{P}, \\ \mathbf{J} &= \sigma \mathbf{E}.\end{aligned}\tag{3.1}$$

Moreover, we assume that no free charges are present, thus

$$\nabla \cdot \mathbf{D} = \rho = 0.\tag{3.2}$$

Then there also can not flow currents from free charges

$$\mathbf{J} = \mathbf{0}.$$

$$\nabla \times \nabla \times \mathbf{E} = \nabla (\nabla \cdot \mathbf{E}) - \Delta \mathbf{E} = -\mu_0 \frac{\partial}{\partial t} (\nabla \times \mathbf{H}).$$

From (3.1), (3.2) and in absence of free carriers, it follows $\nabla \cdot \mathbf{E} = -\nabla \cdot \mathbf{P} / \varepsilon_0 \approx 0$, which is only approximately fulfilled in nonlinear optics due to the nonlinear polarization part. We then obtain

$$\Delta \mathbf{E} - \mu_0 \sigma \frac{\partial}{\partial t} \mathbf{E} - \mu_0 \varepsilon_0 \frac{\partial^2}{\partial t^2} \mathbf{E} = \mu_0 \frac{\partial^2}{\partial t^2} \mathbf{P}.$$

With $\mathbf{P} = \varepsilon_0 \chi^{(1)} \mathbf{E} + \mathbf{P}_{NL}$ and the relative dielectric number $\varepsilon_r = 1 + \chi^{(1)}$ it follows

$$\Delta \mathbf{E} - \mu_0 \sigma \frac{\partial}{\partial t} \mathbf{E} - \mu_0 \varepsilon_0 \varepsilon_r \frac{\partial^2}{\partial t^2} \mathbf{E} = \mu_0 \frac{\partial^2}{\partial t^2} \mathbf{P}_{NL} \quad (3.3)$$

where we assumed, that the linear dielectric susceptibility does not depend on frequency, i.e., the medium is dispersion free.

The **nonlinear wave equation (3.3)** can be solved approximately for the case of plane quasi-monochromatic waves propagating into the positive z -direction:

$$\mathbf{E}(z, t) = \hat{\mathbf{e}} E(z, t) e^{j(\omega t - kz)}, \quad (3.4)$$

$$\mathbf{P}_{NL}(z, t) = \hat{\mathbf{p}} P_{NL}(z, t) e^{j(\omega t - k_p z)}, \quad (3.5)$$

Slowly Varying Envelope Approximation (SVEA)

$$|kE(z, t)| \gg \left| \frac{\partial}{\partial z} E(z, t) \right|, \quad |k_p P_{NL}(z, t)| \gg \left| \frac{\partial}{\partial z} P_{NL}(z, t) \right|, \quad (3.6)$$

$$|\omega P_{NL}(z, t)| \gg \left| \frac{\partial}{\partial t} P_{NL}(z, t) \right|, \quad |\omega E(z, t)| \gg \left| \frac{\partial}{\partial t} E(z, t) \right|. \quad (3.7)$$

Inserting the ansatzes (3.4) and (3.5) in (3.3)

$$\begin{aligned} & \frac{\partial^2 E}{\partial z^2} - 2jk \frac{\partial}{\partial z} E - k^2 E - \mu_0 \sigma \left(j\omega E + \frac{\partial}{\partial t} E \right) \\ & - \mu_0 \varepsilon_0 \varepsilon_r \left(\frac{\partial^2}{\partial t^2} E + 2j\omega \frac{\partial}{\partial t} E - \omega^2 E \right) \\ & = \mu_0 \left(\frac{\partial^2}{\partial t^2} P_{NL} + j\omega \frac{\partial}{\partial t} P_{NL} - \omega^2 P_{NL} \right) (\hat{\mathbf{e}} \cdot \hat{\mathbf{p}}) e^{j(k - k_p)z}. \end{aligned}$$

Employing the dispersion relation $k^2 = \mu_0 \varepsilon_0 \varepsilon_r \omega^2$ the two leading terms cancel, and within the SVEA (3.6),(3.7) it follows

$$2jk \frac{\partial}{\partial z} E + 2j \frac{\omega}{c^2} \frac{\partial}{\partial t} E = -j\omega \mu_0 \sigma E + \mu_0 \omega^2 P_{NL} (\hat{\mathbf{e}} \cdot \hat{\mathbf{p}}) e^{j(k-k_p)z},$$

where we introduced the velocity of light in the linear medium as $c = \sqrt{\mu_0 \varepsilon_0 \varepsilon_r}^{-1}$. We divide this equation by $2jk$ and transform it into a comoving time frame using $t' = t - z/c$, ($z = z'$), and obtain

$$\frac{\partial}{\partial z} E(z, t') = -\alpha E(z, t') - \frac{1}{2} j\omega Z_\omega P_{NL}(z, t') (\hat{\mathbf{e}} \cdot \hat{\mathbf{p}}) e^{j(k-k_p)z}, \quad (3.8)$$

with the damping constant $\alpha = \sigma Z_\omega / 2$ and the impedance of the medium $Z_\omega = \frac{1}{\varepsilon_0 \sqrt{\varepsilon_{r,\omega}} c_0} = \sqrt{\frac{\mu_0}{\varepsilon_0 \varepsilon_{r,\omega}}}$.

Some remarks on

$$\frac{\partial}{\partial z} E(z, t') = -\alpha E(z, t') - \frac{1}{2} j \omega Z_\omega P_{NL}(z, t') (\hat{\mathbf{e}} \cdot \hat{\mathbf{p}}) e^{j(k-k_p)z}, \quad (3.8)$$

- The medium **conductivity σ** leads to **losses** and therefore **damping** of the propagating wave.
- The medium's nonlinear polarization can lead to both **gain or damping**, depending on the **relative phase** between the electric field and the polarization (parametric amplification, frequency conversion, stimulated scattering processes as Raman and Brillouin scattering, multi-photon absorption).
- If the nonlinear polarization is **in phase or in opposite phase** of the electric field, it corresponds to a nonlinear change of the refractive index, leading to a **phase shift of the electric field** (Pockels effect, Kerr effect).
- If the polarization is advancing the field by 90° , the polarization is supplying energy to the field. In the opposite case, the polarization is extracting energy from the field.
- **phase relation is changing during propagation**, if no phase matching of the process, i.e., $k = k_p$, is achieved.