

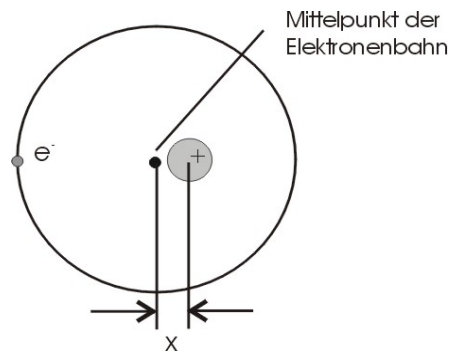
## 2. Nonlinear polarisation

Polarisation is defined as the sum of induced electric dipoles per volume. This optical polarisation is due mostly to the outer valence electrons of a dielectric crystal, which originates from a displacement of the center of negative charge of the electron cloud relative to the much heavier core that is induced by an optical electric field. In the linear case a moderate optical field results in harmonic displacements. In the nonlinear case large displacements may occur, which are not proportional to the inducing optical field.

The model of an elastically bound electron (electronic oscillator) describes very well the area of linear optics, e.g., the dispersion properties  $n(\omega)$ .

### 2.1 Electronic oscillator (linear case)

Let us assume the following one-dimensional electronic oscillator:



$E(t)$  : external field

$x(t)$  : displacement

With the restoring force  $F(t) = -k x(t)$  and damping term  $\sigma \dot{x}(t)$  of the oscillators the equation of motion of an electron with mass  $m$  is

$$\frac{d^2 x(t)}{dt^2} + \sigma \frac{dx(t)}{dt} + \frac{k}{m} x(t) = -\frac{e}{m} E(t) .$$

For the electric field  $E$  and displacement  $x$  we use the Ansatz

$$E(t) = \text{Re}(E_0 \exp(i \omega t)) ,$$

$$x(t) = \text{Re}(x_0 \exp(i \omega t)) .$$

The magnitude of the displacement  $x_0$  depends on frequency  $\omega$ , i.e. it is a function of the spectral distance  $(\omega - \omega_0)$  with the resonance frequency of the electron

$$\omega_0 = \sqrt{k/m} .$$

This results in the differential equation

$$-\omega^2 x_0(\omega) + i \omega \sigma(\omega) + \omega_0^2 x_0(\omega) = -\frac{e}{m} E_0 ,$$

$$\Leftrightarrow (\omega_0^2 - \omega^2) x_0(\omega) + i \omega \sigma x_0(\omega) = -\frac{e}{m} E_0 .$$

For the amplitude we thus obtain

$$x_0(\omega) = \frac{-(e/m) E_0}{\omega_0^2 - \omega^2 + i \omega \sigma} .$$

In the vicinity of the resonance ( $\omega \approx \omega_0$ ) we can use the approximation

$$\begin{aligned} \omega_0^2 - \omega^2 &= (\omega_0 + \omega)(\omega_0 - \omega) \approx 2\omega_0(\omega_0 - \omega) \\ \Rightarrow x_0(\omega \approx \omega_0) &= \frac{-(e/m) E_0}{2\omega_0(\omega_0 - \omega) + i \sigma \omega_0} \end{aligned}$$

The dipole moment of a single electron thus reads

$$\mu(t) = -e x_0(t)$$

The corresponding polarisation of  $N$  oscillators per volume is

$$\begin{aligned} P(t) &= \text{Re}(P_0(\omega) \exp(i\omega t)) \\ P_0(\omega) &= -N e x_0(\omega) \underset{(\omega \approx \omega_0)}{\approx} \left( \frac{N e^2 / m}{2\omega_0(\omega_0 - \omega) + i \sigma \omega_0} \right) E_0 \end{aligned}$$

The susceptibility  $\chi$  describes the relation of polarisation and electric field

$$\begin{aligned} P(\omega) &= \varepsilon_0 \chi(\omega) E(\omega) \\ \text{or} \quad P_0(\omega) &= \varepsilon_0 \chi(\omega) E_0(\omega) \end{aligned}$$

Close to the resonance  $\omega_0$  we find

$$\chi(\omega) = \frac{N e^2}{m \varepsilon_0 (2\omega_0(\omega_0 - \omega) + i \omega_0 \sigma)}$$

or the general result

$$\chi(\omega) = \frac{N e^2}{m \varepsilon_0 ((\omega_0^2 - \omega^2) + i \omega \sigma)}$$

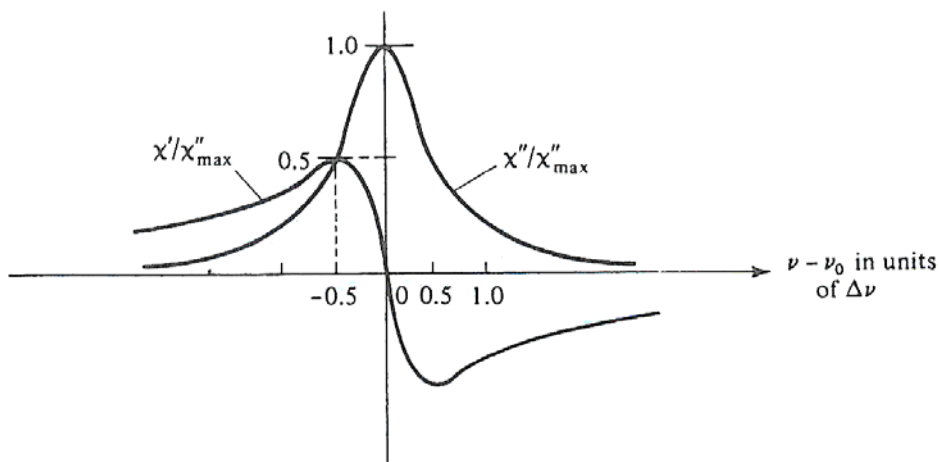
As a consequence  $\chi$  must be a complex quantity

$$\begin{aligned} \chi(\omega) &= \chi'(\omega) - i \chi''(\omega) \quad \text{with } (\chi', \chi'' \in \mathfrak{R}) \\ \Rightarrow P(t) &= \text{Re}(\varepsilon_0 \chi(\omega) E_0 \exp(i\omega t)) \\ &= \varepsilon_0 E_0 \chi'(\omega) \cos(\omega t) + \varepsilon_0 E_0 \chi''(\omega) \sin(\omega t) \end{aligned}$$

the part that is proportional to  $\chi'$  describes the polarisation that is in phase with the electric field, i.e., no energy is transferred in this case. On the other hand,  $\chi''$  describes the polarisation that is shifted by  $\lambda/2$  relative to the driving electric field; as a consequence this part is responsible for absorption of optical radiation and transfers energy to the dielectric medium. Close to the resonance ( $\omega \approx \omega_0$ ) we get

$$\chi'(\omega) = \left( \frac{N e^2}{m \omega_0 \sigma \epsilon_0} \right) \frac{2(\omega_0 - \omega) / \sigma}{1 + 4(\omega - \omega_0)^2 / \sigma^2} \quad \text{dispersion curve}$$

$$\chi''(\omega) = \left( \frac{N e^2}{m \omega_0 \sigma \epsilon_0} \right) \frac{1}{1 + 4(\omega - \omega_0)^2 / \sigma^2} \quad \text{Lorentz curve}$$



The quantities  $\chi'$  (proportional to refractive index) and  $\chi''$  (proportional to absorption) are related to each other by the Kramers-Kronig relations:

$$\chi'(\omega) = \frac{1}{\pi} \text{PV} \int_{-\infty}^{\infty} \frac{\chi''(\omega')}{\omega' - \omega} d\omega' \quad , \quad \chi''(\omega) = -\frac{1}{\pi} \text{PV} \int_{-\infty}^{\infty} \frac{\chi'(\omega')}{\omega' - \omega} d\omega'$$

Here PV means the Cauchy principal value of the integrals that follows. The Kramers-Kronig relations are important for the determination of dielectric function  $\epsilon(\omega)$  and spectral dependence of the refractive index  $n(\omega)$  by measuring the absorption  $\alpha(\omega')$  over a larger spectral region  $\omega'$ .

## 2.2 Optical susceptibility

Now we want to discuss how the resonance at  $\omega_0$  influences the propagation of an optical wave through the dielectric medium:

$$\begin{aligned} \vec{D} &= \epsilon_0 \vec{E} + \vec{P} + \vec{P}_{\text{trans}} = \underbrace{\epsilon \epsilon_0 \vec{E}}_{\text{all other resonances}} + \underbrace{\epsilon_0 \chi(\omega) \vec{E}}_{\text{resonance at } \omega = \omega_0} \\ \Rightarrow \vec{D} &= \epsilon_0 \underbrace{(\epsilon + \chi(\omega))}_{\epsilon'(\omega)} \vec{E} = \epsilon_0 \epsilon'(\omega) \vec{E} \end{aligned}$$

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We assume a wave  $E(z,t) = \text{Re}(E_0 \exp(i\omega t - ik'z))$  with wave number

$$\begin{aligned}
 k' &= \omega \sqrt{\mu_0 \varepsilon_0 \varepsilon'(\omega)} = \omega \sqrt{\mu_0 \varepsilon_0} \sqrt{\varepsilon + \chi(\omega)} \\
 &= \omega \sqrt{\mu_0 \varepsilon_0} \sqrt{\varepsilon} \sqrt{1 + \frac{\chi(\omega)}{\varepsilon}} && \chi(\omega)/\varepsilon \ll 1 \\
 &= \underbrace{\omega \sqrt{\mu_0 \varepsilon_0} n}_k \left( 1 + \frac{1}{2n^2} \chi(\omega) \right) && \sqrt{\varepsilon} \equiv n \\
 &= k \left( 1 + \frac{1}{2n^2} \chi'(\omega) - \frac{i}{2n^2} \chi''(\omega) \right) && \chi = \chi' - i\chi'' \\
 &= k + \Delta k + i\gamma/2
 \end{aligned}$$

As a result, the wave experiences both an absorption  $\gamma$  and an additional phase delay  $\Delta k$ :

$$\begin{aligned}
 \Delta k &= \frac{k}{2n^2} \chi'(\omega) \quad , \quad \gamma = -\frac{k}{n^2} \chi''(\omega) \\
 \Rightarrow E(z,t) &= \text{Re}(E_0 \exp(i\omega t - i(k + \Delta k)z) \exp(\gamma z/2))
 \end{aligned}$$

Here  $\gamma = -\alpha$  is the absorption coefficient

$$\begin{aligned}
 I &= \frac{cn\varepsilon_0}{2} |E|^2 \quad \text{with} \quad |E|^2 = \frac{1}{2} \text{Re}(\vec{E} \cdot \vec{E}^*) \\
 \Rightarrow I(z) &= \underbrace{\frac{cn\varepsilon_0}{2} |E_0|^2}_{I_0} \exp(\gamma z) = I_0 \exp(-\alpha z)
 \end{aligned}$$

This is called the Lambert-Beer law of absorption.

### 2.3 Physical origin of nonlinear polarization

The optical polarisation of dielectric crystals is mostly due to the outer, loosely bound valence electrons that are displaced by the optical electric field

$$P(t) = -Nex(t)$$

Here  $N$  is the density of valence electrons and  $x$  is the deviation of the electrons from the equilibrium position. The form of the energetic potential  $V(x)$  of the electrons reflects the symmetry of the dielectric crystal. For symmetric crystals  $V$  is a symmetric function

$$V(x) = \frac{m}{2} \omega_0^2 x^2 + \frac{m}{4} Bx^4 + \underbrace{\dots}_{\text{higher orders}}$$

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Here  $B$  is a constant and  $\omega_0$  is the resonance frequency of the electronic oscillator. For the restoring force we find

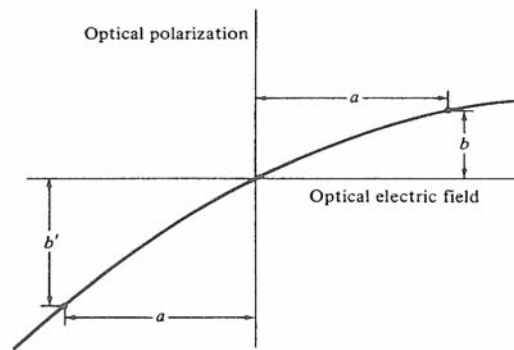
$$F(x) = -\frac{\partial}{\partial x} V(x) = -m\omega_0^2 x - mBx^3 - \dots$$

In crystals that do not have an inversion centre the corresponding potential contains only uneven terms in  $x$

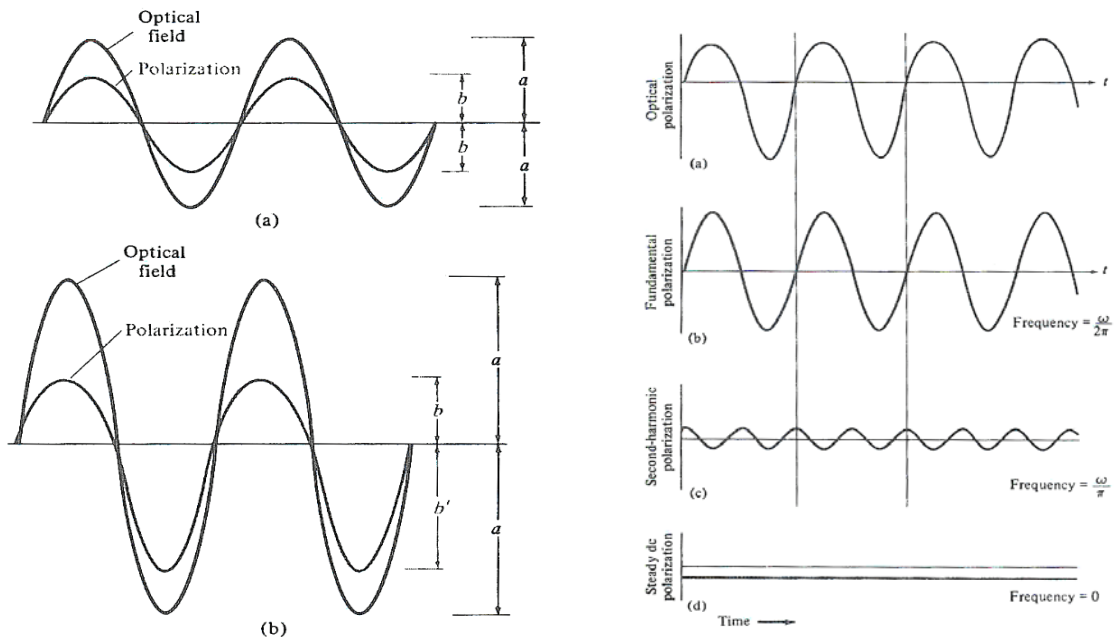
$$V(x) = \frac{m}{2} \omega_0^2 x^2 + \frac{m}{3} Dx^3 + \underbrace{\dots}_{\text{higher orders}}$$

$$\Rightarrow F(x) = -m\omega_0^2 x - mDx^2 - \dots$$

The constants  $B$  and  $D$  are a measure for the magnitude of the involved nonlinearity. We assume a coordinate system where  $D > 0$ . A positive displacement ( $x > 0$ ) results in a larger restoring force, than does the same negative displacement ( $x < 0$ ). It follows that if the force on the electron due to the electric field is positive ( $F = -eE$ , so  $E < 0$ ), the induce polarization is larger than when the field direction is reversed.



Next we consider an alternating electric field  $E(t) = \text{Re}(E_0 \exp(i\omega t))$  applied to the crystal of optical frequency  $\omega$  and amplitude  $a \equiv E_0$ .



The Fourier analysis (right hand side) of the polarisation  $P(t)$  shows contributions with frequencies zero,  $\omega$ , and  $2\omega$ . The relations of the nonlinear polarisation  $P^{(2\omega)}$  and the optical electric field  $E^{(\omega)}$  results from the equation of motion of the electron

$$F = m \ddot{x} ,$$

$$\frac{d^2}{dt^2} + \sigma \frac{d}{dt} + \omega_0^2 x(t) + D x^2(t) = -\frac{e E_0^{(\omega)}}{2m} (\exp(i\omega t) + \exp(-i\omega t)) ,$$

with electric field  $E(t) = E_0^{(\omega)} \cos(\omega t) = 1/2 E_0^{(\omega)} (\exp(i\omega t) + \exp(-i\omega t))$ , damping term  $F_R = -m\sigma \dot{x}$  that accounts for losses, and restoring force  $F = -dV/dx = -\omega_0^2 x + D x^2$ . For the displacement  $x(t)$  we use the Ansatz

$$x(t) = \frac{1}{2} (q_1 \exp(i\omega t) + q_2 \exp(2i\omega t) + c.c.)$$

In this form the static contribution for  $\omega = 0$  is disregarded, however this does not influence the final result. Substituting the last expression into the differential equation gives

$$\begin{aligned} & -\frac{\omega^2}{2} (q_1 \exp(i\omega t) + c.c.) - 2\omega^2 (q_2 \exp(2i\omega t) + c.c.) + \frac{i\omega\sigma}{2} (q_1 \exp(i\omega t) - c.c.) \\ & + i\omega\sigma (q_2 \exp(2i\omega t) - c.c.) + \frac{\omega_0^2}{2} (q_1 \exp(i\omega t) + q_2 \exp(2i\omega t) + c.c.) \\ & + \frac{D}{4} (q_1^2 \exp(2i\omega t) + q_2^2 \exp(4i\omega t) + q_1 q_1^* + q_2 q_2^* + 2q_1 q_2 \exp(3i\omega t) + 2q_1 q_2^* \exp(-i\omega t) + c.c.) \\ & = -\frac{e E_0^{(\omega)}}{2m} (\exp(i\omega t) + c.c.) \end{aligned}$$

This equation must be valid for all times  $t$ , thus the coefficients for oscillations with frequencies  $\omega$  and  $2\omega$  on both sides must be equal. Equating the terms with  $\omega$  gives

$$-\frac{\omega^2}{2} q_1 + \frac{i\omega\sigma}{2} q_1 + \frac{\omega_0^2}{2} q_1 + \frac{D}{4} 2q_1^* q_2 = \frac{-e E_0^{(\omega)}}{2m} .$$

When we assume a small nonlinearity,

$$|D q_2| \ll \sqrt{(\omega_0^2 - \omega^2)^2 + \omega^2 \sigma^2} ,$$

we find the frequency dependence of linear displacement and susceptibility

$$q_1 = -\frac{e E_0^{(\omega)}}{m} \frac{1}{(\omega_0^2 - \omega^2) + i\omega\sigma}$$

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$$\chi^{(\omega)} = \frac{N e^2}{m \varepsilon_0 ((\omega_0^2 - \omega^2) + i \omega \sigma)}$$

When comparing terms with  $2\omega$  we get

$$-2\omega^2 q_2 + i \omega \sigma q_2 + \frac{\omega_0^2}{2} q_2 = -\frac{D}{4} q_1^2$$

$$q_2 = \frac{-D e^2 (E_0^{(\omega)})^2}{2m^2 ((\omega_0^2 - \omega^2) + i \omega \sigma)^2 (\omega_0^2 - 4\omega^2 + 2i \omega \sigma)}$$

The nonlinear polarisation  $P^{(2\omega)}(t)$  at frequency  $2\omega$  reads

$$P^{(2\omega)}(t) = -eN \frac{1}{2} (q_2 \exp(2i\omega t) + c.c.) \equiv \frac{1}{2} (d^{(2\omega)} (E_0^{(\omega)})^2 \exp(2i\omega t) + c.c.)$$

with the nonlinear optical coefficient  $d^{(2\omega)}$ . This coefficient is related by  $d^{(2\omega)} = \varepsilon_0 \chi^{(2\omega)}$  to the susceptibility of second order.

For the amplitude of the nonlinear polarisation  $P_0^{(2\omega)}$  we get

$$P^{(2\omega)}(t) = \frac{1}{2} (P_0^{(2\omega)} \exp(2i\omega t) + c.c.),$$

$$P_0^{(2\omega)} = d^{(2\omega)} E_0^{(\omega)} E_0^{(\omega)}.$$

With this result the nonlinear coefficient  $d^{(2\omega)}$  may be written in the form

$$d^{(2\omega)} = -N e q_2 / (E_0^{(\omega)})^2$$

and by using

$$\chi^{(\omega)} = \frac{N e^2}{m \varepsilon_0 ((\omega_0^2 - \omega^2) + i \omega \sigma)},$$

$$\chi^{(2\omega)} = \frac{N e^2}{m \varepsilon_0 ((\omega_0^2 - (2\omega)^2) + i(2\omega)\sigma)},$$

we finally get

$$d^{(2\omega)} = \frac{m D (\chi^{(\omega)})^2 \chi^{(2\omega)} \varepsilon_0^3}{2 N^2 e^3}$$

This equation relates  $d^{(2\omega)}$  with the linear susceptibilities  $\chi^{(\omega)}$  and  $\chi^{(2\omega)}$  and with the nonlinear coefficient  $D$ . It therefore allows for the theoretical prediction of  $d^{(2\omega)}$ .

## 2.4 Tensor character of nonlinear optical effects

Up to now we only used a scalar treatment of polarisation and electric field. However, for anisotropic crystals we have to take into account the tensor character of susceptibility; thus in a vectorial treatment we find for the  $x$  component of  $P_0^{(2\omega)}$

$$\begin{aligned} P_{0,x}^{(2\omega)} &= d_{xxx}^{(2\omega)} E_{0,x}^{(\omega)} E_{0,x}^{(\omega)} + d_{xyy}^{(2\omega)} E_{0,y}^{(\omega)} E_{0,y}^{(\omega)} + d_{xzz}^{(2\omega)} E_{0,z}^{(\omega)} E_{0,z}^{(\omega)} \\ &\quad + 2d_{xzy}^{(2\omega)} E_{0,z}^{(\omega)} E_{0,y}^{(\omega)} + 2d_{xzx}^{(2\omega)} E_{0,z}^{(\omega)} E_{0,x}^{(\omega)} + 2d_{xxy}^{(2\omega)} E_{0,x}^{(\omega)} E_{0,y}^{(\omega)} \\ &= \sum_{j,k=x,y,z} d_{x,jk}^{(2\omega)} E_{0,j}^{(\omega)} E_{0,k}^{(\omega)}. \end{aligned}$$

The general relation may be written in the form

$$P_i^{(2\omega)} = \sum_{j,k=x,y,z} d_{ijk}^{(2\omega)} E_{0,j}^{(\omega)} E_{0,k}^{(\omega)}.$$

Let us reverse the direction of an electric field that is applied to a centrosymmetric crystal,  $E_0^{(\omega)} \rightarrow -E_0^{(\omega)}$ . The nonlinear polarisation thus reads

$$-P_i^{(2\omega)} = \sum_{j,k} d_{ijk}^{(2\omega)} (-E_{0,j}^{(\omega)}) (-E_{0,k}^{(\omega)}),$$

with the only consequence that  $d_{ijk}^{(2\omega)} = 0$  for all indices  $ijk$ , i.e. centrosymmetric crystals that do not possess an inversion symmetry and thus do not allow for second harmonic generation.

In the literature very often reduced indices of the form  $(ijk) \rightarrow (il)$  are used where the symmetry properties  $d_{ijk} = d_{jik}$  of the nonlinear coefficients have been used. This results in a transformation

$$\begin{array}{lll} 11 \rightarrow 1 & 22 \rightarrow 2 & 33 \rightarrow 3 \\ 23, 32 \rightarrow 4 & 13, 31 \rightarrow 5 & 12, 21 \rightarrow 6 \end{array}$$

for example  $d_{311} \rightarrow d_{31}$ ,  $d_{222} \rightarrow d_{22}$  and  $d_{131} \rightarrow d_{15}$ .

Symmetry operations (e.g., mirror planes of rotation axes) reduce the number of independent coefficients of the tensor  $\hat{d}$ , i.e. there is a limited number of coefficients with  $d_{ijk} \neq 0$ .

As can be seen in the following table, for many crystals the nondiagonal elements (which involve different polarization components of the incident light) of the  $\hat{d}$  tensor are the dominating coefficients.



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**Table 8-1** The Nonlinear Optical Coefficients of a Number of Crystals\*

| Crystal   | $d_{ijk}^{(2\omega)}$ in Units of $1/9 \times 10^{-22}$ MKS                            |
|---|--|
| LiIO <sub>3</sub>                                       | $d_{15} = 4.4$   |
| NH <sub>4</sub> H <sub>2</sub> PO <sub>4</sub><br>(ADP) | $d_{36} = 0.45$<br>$d_{14} = 0.50 \pm 0.02$  |
| KH <sub>2</sub> PO <sub>4</sub><br>(KDP)                | $d_{36} = 0.45 \pm 0.03$<br>$d_{14} = 0.35$  |
| KD <sub>2</sub> PO <sub>4</sub>                         | $d_{36} = 0.42 \pm 0.02$<br>$d_{14} = 0.42 \pm 0.02$                                   |
| KH <sub>2</sub> ASO <sub>4</sub>                        | $d_{36} = 0.48 \pm 0.03$<br>$d_{14} = 0.51 \pm 0.03$                                   |
| Quartz  | $d_{11} = 0.37 \pm 0.02$   |
| AlPO <sub>4</sub>                                       | $d_{11} = 0.38 \pm 0.03$   |
| ZnO   | $d_{33} = 6.5 \pm 0.2$<br>$d_{31} = 1.95 \pm 0.2$<br>$d_{15} = 2.1 \pm 0.2$            |
| CdS   | $d_{33} = 28.6 \pm 2$<br>$d_{31} = 30 \pm 10$<br>$d_{36} = 33$<br>$d_{14} = 80 \pm 14$ |
| GaP   | $d_{14} = 80 \pm 14$   |
| GaAs  | $d_{14} = 72$  |
| BaTiO <sub>3</sub>                                      | $d_{33} = 6.4 \pm 0.5$<br>$d_{31} = 18 \pm 2$<br>$d_{15} = 17 \pm 2$                   |
| LiNbO <sub>3</sub>                                      | $d_{15} = 4.4$<br>$d_{22} = 2.3 \pm 1.0$   |
| Te  | $d_{11} = 517$   |
| Se  | $d_{11} = 130 \pm 30$  |
| Ba <sub>2</sub> NaNb <sub>5</sub> O <sub>15</sub>       | $d_{33} = 10.4 \pm 0.7$<br>$d_{32} = 7.4 \pm 0.7$                                      |
| Ag <sub>3</sub> AsS <sub>3</sub><br>(proustite)         | $d_{22} = 22.5$<br>$d_{36} = 13.5$   |
| CdSe  | $d_{31} = 22.5 \pm 3$  |
| CdGeAs <sub>2</sub>                                     | $d_{36} = 363 \pm 70$  |
| AgGaSe <sub>2</sub>                                     | $d_{36} = 27 \pm 3$  |
| AgSbS <sub>3</sub>                                      | $d_{36} = 9.5$   |
| ZnS   | $d_{36} = 13$  |

\*Some authors define the nonlinear coefficient  $d$  by  $P = \epsilon_0 d E^2$  rather than by the relation  $P = d E^2$  used here.