

## Module 3 : Nonlinear susceptibilities of materials

### Lecture 17 : Nonlinear Optical Materials

#### Objectives

#### In this lecture you will learn the following

- Introduction to nonlinear materials.
- Ferroelectric crystals.
- Semiconductors- bound and mobile carrier nonlinearities.
- Current trends.

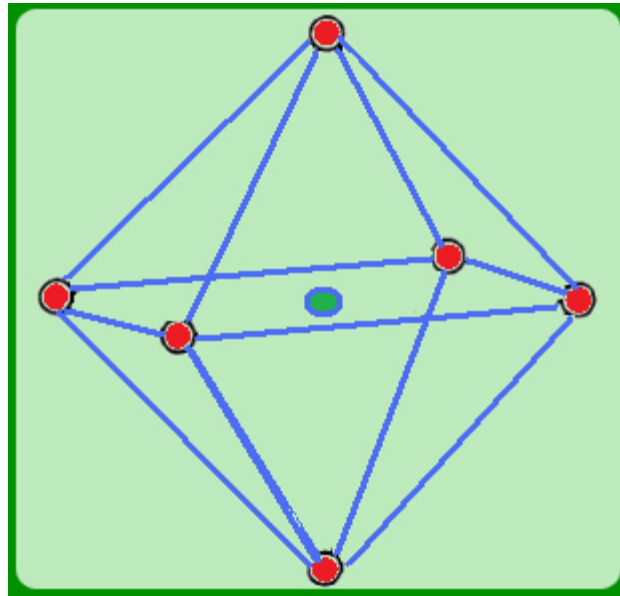
Right from the initial days it was realized that nonlinear optical effects provide a means of constructing new devices. The earliest nonlinear optical materials were inorganic crystals - usually those materials for which crystals in reasonably good optical quality and size ( $\sim 1 \text{ cm}^3$ ) available. The earliest guide in the search for nonlinear optical materials was provided by Miller's rule discussed earlier in Lecture 7 which related the second order susceptibility  $\chi^{(2)}$  with  $\chi^{(1)}$  through

$$\chi_{ijk}^{(2)}(\Omega, \omega_1, \omega_2) = \Delta_{ijk} \chi_{ii}^{(1)}(\Omega) \chi_{jj}^{(1)}(\omega_1) \chi_{kk}^{(1)}(\omega_2)$$

The Miller's delta  $\Delta_{ijk}$  was found to be nearly independent of material. The scope of search for new nonlinear optical materials broadened enormously- first, by the development of the powder second harmonic generation method by Kurtz and Perry [SK Kurtz and T. T. Perry. "A powder technique for the evaluation of nonlinear optical materials." J. Appl. Phys. **39**, 3798 (1968)] and later by the discovery of the optical Kerr shutter [M A Duguay, and J. W. Hansen, Appl. Phys. Lett. 15, 192 (1969)], degenerate four wave mixing (DFWM) and the Z-scan methods discussed in later lectures. The main application driving the search for third order nonlinear optical materials is "all optical logic" and switching while for second order materials it remains frequency conversion, specially of coherent sources based on semiconductor diode lasers. We discuss the nonlinear response of these materials in 3 categories- ferroelectrics and semiconductors in this lecture and organic materials in the next.

#### OXIDE NONLINEAR OPTICAL CRYSTALS:

Most of these crystals are ferroelectric although they are not always used in their ferroelectric phase. On the otherhand the ferroelectric property has been crucial in poling them for quasi-phase-matching. The nonlinear polarizable unit in many of these crystals such as  $\text{LiNbO}_3$  and  $\text{LiTaO}_3$  are the oxygen octahedra shown in Figure 17.1 below.



**Figure 17.1 Oxygen octahedron –the basic building block of many nonlinear optical ferroelectric crystals ( red circles: oxygen atoms, green circle cation)**

The position of the central B cation atom becomes unstable at temperatures below the Curie Temperature. Once this atom moves off centre the above unit acquires a non-vanishing hyperpolarizability  $\beta$ . The polarizability is largely due partially delocalized p electrons of oxygen atoms. These are perturbed by the displacement of the B cation atoms. One can then relate  $\beta_{ijk}$  and hence  $\chi^{(2)}$

to the ionic displacement. This provided the first understanding of nonlinear response of these crystals. [M. DiDomenico, and S. H. Wemple. J. Appl. Phys. **40**,720 (1969)]. By now several first principle band structure based calculations have been reported for nonlinear susceptibility  $\chi^{(2)}$  based on sum over states expressions. It is fair to say that theory of nonlinear susceptibility for crystals has not played a crucial role in the development of new second order inorganic crystals. In part, this is due to the fact often other requirements like phase-matchability, transparency range and the potential to grow good crystals in the required size are often more crucial.

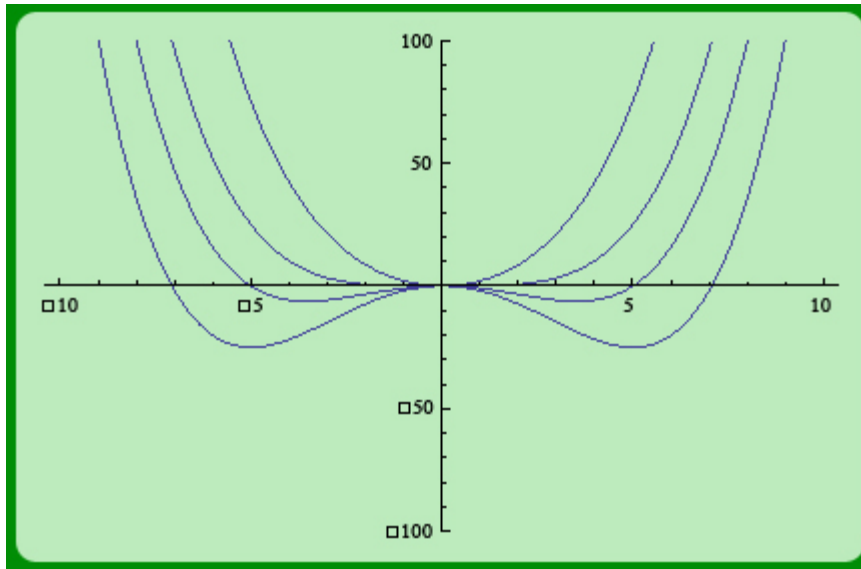
For example beta Barium Borate has a relatively small  $\chi^{(2)}$  ( $d_{22} \sim 2.6 \text{ pm/V}$  compared to  $d_{33} \sim 27 \text{ pm/V}$  for  $\text{LiNbO}_3$ ). Yet, it is an excellent nonlinear optical crystal because it is transparent well into the ultraviolet region, has a high damage threshold and is phase-matchable over a wide spectral range and is a robust crystal. The hyperpolarizability  $\beta$  for each unit can be estimated by simpler LCAO models providing reasonably satisfactory results.

### Periodic Poling:

All displacement ferroelectrics are susceptible to form domains of various sizes and geometries. To form large size useful nonlinear crystals they need to be uniformly poled for applications involving birefringent phase matching and periodically poled for quasi-phase matching. The field required to reverse the dipole moment is called the coercive field.

To understand the basics of ferroelectric crystals and poling it is very instructive to look at their vibrational energy as a function of a suitable mode called soft mode whose frequency goes to zero at the curie temperature. We can then model the corresponding oscillator energy as

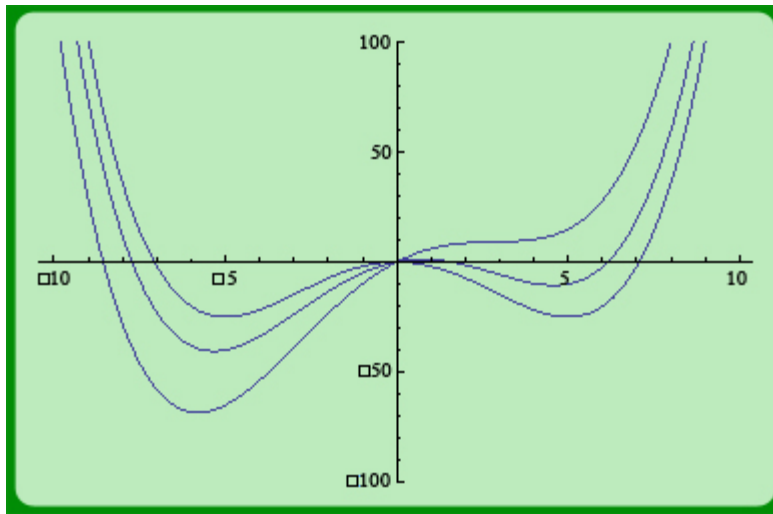
$$\mathcal{E} = k_0 x^2 (T - T_C) / T_C + Bx^4$$



**Figure 17.2 Potential energy for an anharmonic oscillator with a soft mode**

For  $T > T_C$ , the energy has only one minimum at the origin. As  $T$  approaches  $T_C$ , this becomes a shallower minimum implying decreasing vibrational mode frequency. For  $T < T_C$  there are two minima lower in energy than the one at origin. Then the crystal distorts itself to a new configuration with a dipole moment in each unit cell. This could be either of the two minima corresponding to two possible configurations with dipole moments in opposite directions. As the temperature lowers the minima get deeper. If we now apply an electric field it changes the potential energy to (figure 17.3)

$$\mathcal{E} = k_0 x^2 (T - T_C) / T_C + Bx^4 + E.x$$



**Figure 17.3 Potential energy for an anharmonic oscillator with a soft mode in the presence of an electric field**

Now, as we increase the field one minimum gets shallower and shallower till it disappears completely and only one minimum is left. Thus, a electric field applied in appropriate direction can change the direction of the dipole polarization. Obviously if the temperature is closer to the Curie Temperature the minima are shallower and it will need smaller fields to change the polarity of the crystal.

### Semiconductors:

Estimating nonlinear response of semiconductors is a challenging and potentially very rewarding problem because of great advances in epitaxial growth techniques provide a great scope for designing a large variety of materials. We first consider the bulk homogenous semiconductors such as GaAs. The first problem is that in semiconductors we have mobile carriers –electrons in the conduction band and holes in the valence band in addition to the polarizable valence electrons which can be treated the same way as in molecular solids. The wave functions of these electrons are not localized and so matrix elements of the displacement operator are inappropriate. One has then to use the so called A.P representation for the electric field. Representing the vector potential by  $\vec{A}$ , the Hamiltonian including the field is given by:

$$H = \sum_{i=1}^N \left( \frac{(\vec{p}_i - e\vec{A})^2}{2m} + V(x_i) \right) + \sum_{i < j=1}^N \frac{e^2}{|\vec{r}_i - \vec{r}_j|} \quad (17.1)$$

corresponding to the unperturbed Hamiltonian

$$H_0 = \sum_{i=1}^N \left( \frac{|\vec{p}_i|^2}{2m} + V(x_i) \right) + \sum_{i < j=1}^N \frac{e^2}{|\vec{r}_i - \vec{r}_j|} \quad (17.2)$$

Early attempts to calculate nonlinear susceptibilities were hampered by the lack of reliable description of the unperturbed states. Since most of the experimental information is in the transparency region of the crystal, unlike the linear response one cannot identify any critical points in the spectra. Still it was soon clear that nonlinear susceptibilities involve much more detail than what was obtained from linear spectra. For example, already in 1963 Butcher and Mclean [Butcher, P. N., and T. P. McLean. "The non-linear constitutive relation in solids at optical frequencies." *Proceedings of the Physical Society* 81.2 (1963): 219.] exploited the similarity between the  $\vec{A}\vec{P}$  perturbation with the  $\vec{k}\cdot\vec{p}$  perturbation to describe the dispersion of energy bands showed that mobile carriers in a partially filled band contribute a nth order nonlinear susceptibility

$$\chi^{(n)} \sim \frac{1}{\omega^{n+1}} \frac{\partial^{n+1} \epsilon}{\partial k^{n+1}} \quad (17.3)$$

This nonlinearity will obviously get more important at lower frequencies. Indeed it was experimentally discovered by Patel et al [C. K. N.Patel, R. E. Slusher, and P. A. Fleury Phys Rev Lett **17**,1011 (1966)] in 4 wave mixing experiments using CO<sub>2</sub> laser operating in the mid infrared and found to be well described by the well known Kane's model for nonparabolic bands in InSb [EO Kane J.Phys.Chem Solids **1**,249 (1957)]. In contrast, it was shown that that Kane's model for the band structure of small gap

III-V compounds gives a nonzero contribution to  $\chi^{(2)}$  only when the spin orbit coupling is fully included. [K.C.Rustagi, J.Phys.Chem Solids **30**,2547(1969)]. This was a bit surprising at first since the model does provide a very good description of  $\chi^{(1)}$  as well as the mobile carrier contribution to  $\chi^{(3)}$ . However, on further thinking this seems very reasonable since Kane's model does not involve any parameter directly involving inversion asymmetry. The bound electron contribution could be calculated in tight binding orbitals for the covalent bonds. [S S Jha and N.Bloembergen Phys Rev **171**,891(1968), C.Flytzanis and J.Ducuing Phys Rev **178**,1218(1969)]. Another attractive model due to Levine [B.F. Levine Phys Rev **B7**,2600(1973)] describes the bond polarizability in terms of the anharmonic motion of the bond charge.

#### MOBILE CARRIER NONLINEARITY:

A very interesting way to look at the mobile carrier contribution, is to start with the linear dielectric function contribution by mobile carriers given by

$$\epsilon(\omega)/\epsilon_0 = \epsilon(\infty)/\epsilon_0 - \frac{\omega_p^2}{\omega^2 + i\omega\gamma} \quad (17.4)$$

where  $\epsilon(\infty)$  is the low frequency limit of dielectric function due to electrons with

$$\omega_p^2 = Ne^2/m^* \epsilon_0 \quad (17.5)$$

$m^*$  is the effective mass and  $\gamma$  is the collision frequency or the inverse of the collision time.

(This convention of calling the low frequency limit as may seem strange –it is due to fact that we are looking at dielectric function at frequencies much larger than phonon frequencies and much smaller than electronic resonances.) Now, if the band dispersion is nonparabolic say as given by the Kane's model,

$$E_{ck} = (E_g/2) \left( \sqrt{1 + \frac{2\hbar^2 k^2}{m^* E_g}} - 1 \right) \quad (17.6)$$

Clearly, the effective mass  $m^* = \hbar^2 / (\partial^2 E / \partial k^2)$  becomes  $k$  dependent. Expanding the square root term

we can see that the next higher order term goes like  $\sim k^4$ . It follows from this model that nonparabolicity becomes important for narrow gap semiconductors like InSb. To calculate the nonlinear response of carriers in a nonparabolic band one can start with the Boltzmann transport equation for the distribution function  $f(\vec{k}, t)$ , the probability density of occupation of a state  $\vec{k}$  at time  $t$ . For a uniform

medium  $f(\vec{k}, t)$  satisfies the equation

$$\frac{\partial f}{\partial t} - (e/\hbar) \vec{E} \cdot \nabla_{\vec{k}} f = \left( \frac{\partial f}{\partial t} \right)_{coll} \quad (17.7)$$

where  $E$  is the optical electric field and the the term on the right hand side represents the collision term which depends on various scattering mechanisms. That the relaxation mechanisms depend on the symmetry of the perturbation in  $f$  is obvious at least to the extent that an isotropic perturbation in  $f$  can relax only by inelastic scattering mechanisms while uniaxial symmetry perturbation can relax towards an isotropic  $f$  even by elastic collisions. In very pure high crystalline quality semiconductors isotropic or energy relaxation times are atleast two orders of magnitude larger than momentum relaxation time. In general, we expand  $f$  in spherical harmonics:

$$f(\vec{k}, t) = \sum_{l,m} f_{lm}(\epsilon) Y_{lm}(\theta, \phi) \quad (17.8)$$

where  $Y_{lm}(\theta, \phi)$  are the spherical harmonics and  $(\theta, \phi)$  are the angular coordinates of  $\vec{k}$ , and  $\epsilon$  denotes carrier energy which is taken to be an isotropic function of  $\vec{k}$ . The collision integral is then expanded as

$$\left( \frac{\partial f}{\partial t} \right)_{coll} = - \sum_{lm} \nu_l (f_{lm} - f_{00}^{(0)}) Y_{lm}(\theta, \phi) \quad (17.9)$$

where  $f_{00}^{(0)}$  is the equilibrium distribution function. The subscripts 00 remind us that it is isotropic. One can then solve the transport equation in successively higher orders by expanding  $f$  in a perturbation series in the electric field  $E$ . The third order susceptibility is given by

$$\chi_{xxx}^{(3)}(\omega_1, \omega_2, \omega_3) = \frac{4e^4}{3\varepsilon_0 \pi^2 \hbar^4 (i\omega)} \sum_{\text{permutations}} \frac{1}{6} P(\omega_1, \omega_2, \omega_3) \int_0^\infty dk^2 g_1(\omega_1) f^{(0)'} \quad (17.10)$$

$$[(k^3 [(2/3)g_0(\omega_1 + \omega_2) + (8/15)g_2(\omega_1 + \omega_2)] [\mathcal{E}' g_1(\omega)]')' + k^3 g_0'(\omega_1 + \omega_2) \mathcal{E}' g_1(\omega)]$$

where  $\omega = \omega_1 + \omega_2 + \omega_3$ ,  $g_i(\omega) = 1/(\nu_i - \omega)$  and prime denotes differentiation with respect to  $k^2$ .

This includes three contributions- one due to non-parabolicity(NP) of the band dispersion, second due to energy dependence of relaxation times or collision frequencies and third due to a combination of both these mechanisms. This can be made explicit by writing

$$\chi^{(3)} = \chi^{(3)NP} + \chi^{(3)SC} + \chi^{(3)NS} \quad (17.11)$$

and then obtaining explicit expressions for the three parts. [K.C.Rustagi, Phys rev.B2,4053(1970)]. One important result from the systematic inclusion of relaxation mechanisms is that the nonparabolicity contribution to  $\chi_{xxx}^{(3)}(\omega_a, \omega_a, -\omega_b)$  shows an enhancement as the difference frequency  $\omega_a - \omega_b \rightarrow 0$ .

This is a very important general feature of nonlinear susceptibilities and occurs because several contributions add algebraically to produce a susceptibility and many of them cancel each other. Scattering being a random process spoils this cancellation and thus gives rise to resonances which cancel in absence of scattering. To see this explicitly consider two contributions involved in

$$\chi_{xxx}^{(3)NP}(\omega_a, \omega_a, -\omega_b):$$

$$\sim \frac{1}{\nu_0 - i(\omega_a - \omega_b)} \left( \frac{1}{\nu_1 - i\omega_a} + \frac{1}{\nu_1 + i\omega_b} \right)$$

This obviously goes to zero if we put  $\nu_1 = 0$  and then let  $\omega_a \rightarrow \omega_b$  i.e. the two contributions cancel. If, however,  $\nu_1 \neq 0$  this contribution has a resonant enhancement as  $\omega_a \rightarrow \omega_b$ . This was indeed predicted to be the case for mobile carrier nonlinearity in InSb [K.C.Rustagi, Phys rev.B2,4053(1970)and] and was subsequently verified in experiments several years later [S.Y.Yuen, and P. A. Wolff. Appl Phys Lett, 40,457(1982), K.C.Rustagi, Appl Phys Lett44,1121 (1984) ].

Instead of solving the transport equation one can also use the kinetic equations for average momentum  $p$  and average kinetic energy  $W$  as:

$$\dot{p} + \frac{p}{\tau_m} = -eE \quad (17.12)$$

with  $\tau_m$ , as the momentum relaxation time i.e, if the electron distribution is given a drift momentum it relaxes exponentially to zero with a relaxation time of  $\tau_m$ . We write collision frequency as

$$\nu_m = 1/\tau_m \quad (17.13)$$

The corresponding equation for carrier energy  $W$  is

$$\delta \dot{W} + \frac{\delta W}{\tau_{th}} = \frac{-eE.p}{m} \quad (17.14)$$

with  $\tau_m$  denoting the energy relaxation time.

We demonstrate this by calculating  $\chi_{xxx}^{(3)NP}(\omega_a, \omega_a, -\omega_a)$  corresponding to the nonlinear refraction. If the laser electric field is represented by

$$E = E_\omega e^{-i\omega t} + \text{complex conjugate (cc)}$$

we obtain

$$p = \frac{eE_\omega e^{-i\omega t}}{(i\omega - \nu_m)} + C.C. \quad (17.15)$$

and

$$(\delta W)_0 = \tau_{th}(-e/m)(E.p)\left(\frac{1}{i\omega - \nu_m} - \frac{1}{i\omega + \nu_m}\right) \quad (17.16)$$

Now, because of energy dependence of the scattering process this implies

$$\delta W \Rightarrow \delta v_m = \delta W \cdot \frac{\partial v_m}{\partial W} \quad (17.17)$$

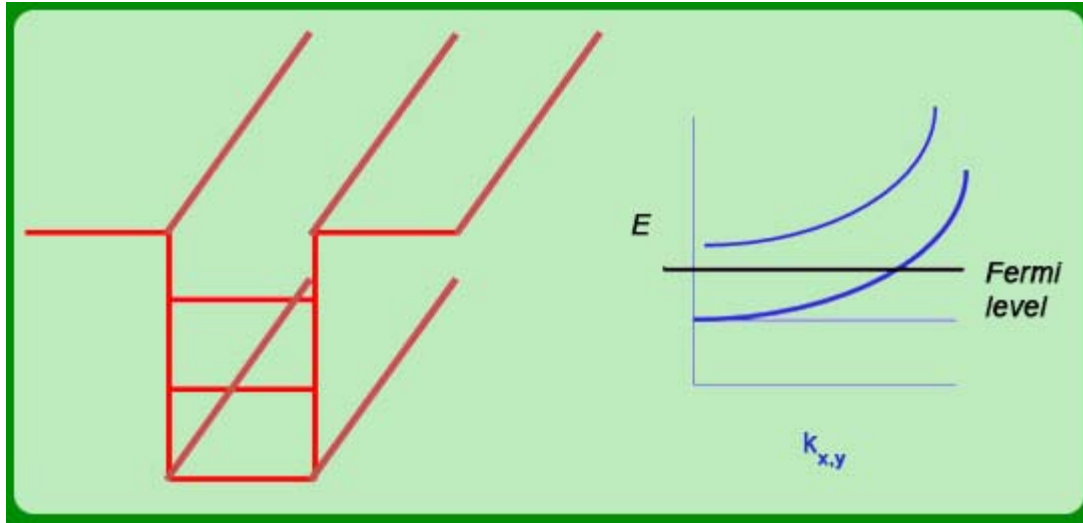
and finally we get the intensity dependent dielectric function as

$$\delta \epsilon = i \frac{\omega_p^2}{\omega^5} \frac{e^2}{m} \frac{v_m^2}{E_F} \tau_{th} |E|^2 \sim \frac{1}{\alpha^2 \omega^5}$$

Clearly, these nonlinearities become very important in the far infra-red. [ See, e.g., A. Mayer, and F. Keilmann. Phys Rev B **33**,6962 (1986) as an early example] and THz regimes.

### Quantum Size Effects:

Epitaxial growth techniques have provided a means of making semiconductor materials by design. The simplest of these the quantum wells are formed by sandwiching a smaller band gap semiconductor between two larger gap materials. For example GaAs in AlAs. The potential energy then looks like:



**Figure 17.5 energy bands in a semiconductor quantum well**

Motion of electrons in the conduction band or of the hole in the valence band can be treated like that of an electron with an effective mass  $m^*$ . Then the energy levels are quantized in the direction of growth i.e. normal to the plane forming the interface. This is then the particle in a well problem and the corresponding structures are called quantum well. This quantization effects the nonlinear response of the material qualitatively and many devices are based on such structures. Here we restrict ourselves to just noting that now the energy band splits into several sub bands and inter-sub-band transitions become possible across the Fermi level. These transitions have large oscillator strengths and give rise to strong nonlinearities.

### Recap

#### In this lecture you have learnt the following

- Nonlinear response of ferroelectric crystals can be modeled in terms of oxygen octahedra and the unit cell dipole moment.
- Periodic poling can be understood in a simple model of displacive ferroelectrics.
- Semiconductors have bound electron response- understood in terms of LCAO models.
- And mobile carrier response understood in terms of Boltzmann transport equation.
- Mobile carrier nonlinearity grows many orders of magnitude at THz frequencies.
- Quantum confinement of carriers gives another tool- the inter-sub band resonances- to engineer the nonlinear response of semiconductors.