THE NON-LINEAR OPTICAL PROPERTIES OF CRYSTALS AND MOLECULES

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by

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ABSTRACT

We consider some of the factors which affect the magnitudes of the tensor coefficients describing the nonlinear optical effects of second-harmonic generation and the Pockels or linear electro-optic effect. The effects of molecular geometry are our particular concern. The electro-optic coefficients of double sulphates with the langbeinite structure are compared with those of tetragonal phosphates and arsenates by ascribing the nonlinearities to the XO_4 tetrahedra. The unfavourable orientation of the SO_4 groups is shown to be responsible for the low electro-optic coefficients of the langbeinites.

These ideas are carried a stage further by assigning the nonlinearities to individual bonds. By this means the signs and magnitudes of the second-harmonic generation coefficients of several niobates are predicted from those of lithium niobate. Similar calculations are carried out for iodates, and empirical nonlinear optical bond polarisabilities are evaluated for a number of complex materials containing covalently bonded oxygen atoms. It is shown that the nonlinear polarisability depends on the electronegativity difference between the atoms forming the bond, and on their coordination.

A further chapter uses the well-known anharmonic oscillator model to establish a connection between nonlinear optical effects and optical activity in crystals of sodium chlorate and sodium bromate.

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Chapter 1

INTRODUCTION

Nonlinear optical coefficients

Nonlinear optics is concerned with the response of material media to strong electromagnetic fields, when some, but not necessarily all, of the fields are associated with light waves. Historically, it is convenient to divide nonlinear optical (NLO) effects into two categories. In the first group, strong d.c. electric or magnetic fields alter the refractive index of a substance. The Kerr and Faraday effects are typical of these phenomena, most of which were discovered in the second half of the last century. The advent of the laser heralded the discovery of the second category, where the intense light beam itself provides the strong electromagnetic fields, giving rise to effects such as second-harmonic generation[1] (SHG) and optical rectification[2]. When these phenomena are incorporated into electromagnetic theory by means of nonlinear constitutive relations, this distinction becomes the trivial one of dispersion, analogous to the linear case, where $\chi = (\epsilon - 1)$ at d.c. and radio frequencies and $(n^2 - 1)$ at optical frequencies.

The interaction between nondissipative media and time-varying electromagnetic fields can be described by

a time-averaged energy function[3]. The tensors that describe NLO effects can be derived from this function, which may be written in tensor notation as a power series in the field strengths:

$$-\tfrac{1}{\epsilon_0}F = \tfrac{1}{2}\underline{\underline{\chi}}:\underline{\mathcal{E}}\underline{\mathcal{E}} + \tfrac{1}{3}\underline{\underline{\underline{\chi}}}:\underline{\mathcal{E}}\underline{\mathcal{E}}\underline{\mathcal{E}} + \ldots \quad \text{(electric dipole effects)}$$
$$+\tfrac{1}{2}\underline{\underline{\chi}}:\underline{\mathcal{E}}\mathcal{H} + \tfrac{1}{3}\underline{\underline{\underline{\chi}}}:\underline{\mathcal{E}}\underline{\mathcal{E}}\mathcal{H} + \ldots \quad \text{(magnetic dipole effects)}$$
$$+\tfrac{1}{2}\underline{\underline{\chi}}:\underline{\mathcal{E}}\nabla\underline{\mathcal{E}} + \tfrac{1}{3}\underline{\underline{\underline{\chi}}}:\underline{\mathcal{E}}\underline{\mathcal{E}}\nabla\underline{\mathcal{E}} + \ldots \quad \text{(elec. quadrupole effects)}$$
$$+ \text{ higher order terms.} \qquad \text{- - - (1.1)}$$

Our interest centres on the electric dipole effects, which generate a polarisation

$$\underline{P} = -\frac{\partial F}{\partial \underline{\mathcal{E}}} = \epsilon_0(\underline{\underline{\chi}}\cdot\underline{\mathcal{E}} + \underline{\underline{\underline{\chi}}}:\underline{\mathcal{E}}\underline{\mathcal{E}} + \ldots). \qquad \text{- - - (1.2)}$$

The magnitude of the susceptibilities χ can be estimated by assuming that each term induces a dipole moment of order ea_0 per atom when $\mathcal{E}$ is of the order of atomic field strengths $\mathcal{E}_{at} = e/4\pi\epsilon_0 a_0^2 \simeq 10^{12}$ V m^{-1}. Thus χ is of order unity and each successive susceptibility is smaller by a factor of $\mathcal{E}_{at}^{-1}$. This puts the first-order nonlinearity within easy reach of experimental measurement. In the linear electro-optic effect (LEO), a moderate field of 10^6 V m^{-1} (1kV across a 1mm crystal) produces a detectable change of at least a few parts per million in refractive index. At optical frequencies, field strengths sufficient to ionise air are attained in focused beams from high power pulsed lasers, although

such intensities are far in excess of those normally used to generate the second harmonic of light. The next term is responsible for the Kerr effect and third-harmonic generation: both are readily observable.

This thesis is concerned with the linear electro-optic effect and second-harmonic generation, which are both special cases of the process in which two fields $E_j^{\beta} e^{i\beta t}$ and $E_k^{\gamma} e^{i\gamma t}$ generate a polarisation

$$P_i^{\alpha} e^{i\alpha t} = \epsilon_0 \chi_{ijk}^{\alpha\beta\gamma} E_j^{\beta} e^{i\beta t} E_k^{\gamma} e^{i\gamma t}, \qquad \text{- - - (1.3)}$$

where $\alpha = \beta + \gamma$, and summation over repeated indices is implied. In the electro-optic effect, $\alpha = \beta$ and $\gamma = 0$; in SHG, $\alpha = 2\beta = 2\gamma$. In equation (1.3) we have used a convention, introduced by Pershan[3,4], of writing the Fourier components of a field at frequency ω as $(\underline{E}^{\omega} e^{i\omega t} + \underline{E}^{\omega *} e^{-i\omega t})$. This notation has the advantage of simplifying theoretical calculations, but disadvantages in computing numerical quantities. For this reason it has not been adopted by experimental workers. The real amplitude of the wave is $2|\underline{E}|$, or $|\underline{E}|$ is half that of the usual definition. This leaves the linear susceptibility unchanged, but introduces a factor of two into the lowest-order nonlinearity, and further factors of two into higher-order terms. In experimental work it is customary to denote the nonlinear susceptibility by d, and the fields by $\underline{E}\cos\omega t$. Thus

$d^{2\omega}_{ijk} = \frac{1}{2}\chi^{2\omega\omega\omega}_{ijk}$ (see the appendix in Robinson[5]). There is a further complication in the electro-optic effect. Here we are considering the limit as $\gamma \to 0$ of both sum- and difference-frequency generation, i.e. (1.3) and

$$P^{\alpha}_{i} e^{i\alpha t} = \epsilon_{o} \chi^{\alpha\beta\gamma}_{ijk} E^{\beta}_{j} e^{i\beta t} E^{\gamma *}_{k} e^{-i\gamma t}, \qquad - - - (1.4)$$

where $\alpha = \beta - \gamma$. This introduces another factor of two, so that $d^{\omega}_{ijk} = \chi^{\omega\omega 0}_{ijk}$.

Symmetry considerations

The third-rank tensor χ_{ijk} necessarily vanishes in centrosymmetric crystals[6]. The suffices i,j,k may be permuted at will, provided that the frequencies are permuted simultaneously so that a given frequency is always associated with the same index[3,7]. In both LEO and SHG two frequencies are identical, making d^{ω}_{ijk} symmetric in the first two indices, and $d^{2\omega}_{ijk}$ symmetric in the last two. This additional symmetry reduces the number of independent tensor elements from 27 to 18, and permits the contraction of the indices according to Voigt's[8] scheme: 11 → 1; 22 → 2; 33 → 3; 23,32 → 4; 31,13 → 5; 12,21 → 6. Thus the LEO coefficients may be represented by a 6 x 3 matrix d_{pk} ($p = 1 \to 6$, $k = 1 \to 3$), and the SHG coefficients by a 3 x 6 matrix d_{ip}.

The symmetry elements of each of the 32 point groups can be used to establish the nonvanishing

coefficients for each crystal class[6]. For example, the inversion operation requires that $\chi_{ijk} = -\chi_{ijk}$, so that all coefficients are identically zero in centrosymmetric crystals. Crystal symmetry subjects the nonvanishing coefficients to additional interrelationships which are identical for the SHG and piezoelectric tensors. When these tensors are represented by matrices, however, one small difference arises. The factors of two which appear in the piezoelectric matrices for some of the trigonal and hexagonal crystal classes are absent in the SHG matrices. This is because the piezoelectric matrix operates on a "vector" $(\sigma_{xx}, \sigma_{yy}, \sigma_{zz}, \sigma_{yz}, \sigma_{zx}, \sigma_{xy})$ whereas the SHG matrix operates on $(E_x^2, E_y^2, E_z^2, 2E_yE_z, 2E_zE_x, 2E_xE_y)$. Bearing this distinction in mind, the tabulations[6] of piezoelectric matrices serve also for the SHG matrices. The allowed LEO coefficients are simply given by the transposed SHG matrices.

Kleinman[9] has shown that the SHG tensor exhibits even greater symmetry when both the frequencies involved are well removed from the electronic and ionic absorption regions so that dispersion can be neglected. Kleinman's symmetry condition, which follows from the assumption of an energy function and implies that χ_{ijk} is invariant under any permutation of indices, has been found experimentally to hold. The SHG matrices for the

acentric point groups, reduced in accordance with Kleinman's rule, have been tabulated by Bechmann and Kurtz[10].

The electro-optic effect is often described by the tensor r_{ijk} (sometimes z_{ijk}), or its contracted form r_{pk}. These coefficients are defined in terms of the electric-field-induced changes of the refractive index ellipsoid[6]:

$$\left[(1/n^2)_{ij} + r_{ijk}\mathcal{E}_k\right] x_i x_j = 0. \qquad \text{- - - (1.5)}$$

The relationship between r_{ijk} and d_{ijk} is[11],

$$d_{ijk} = -n_{il}^2 n_{jm}^2 r_{lmk}. \qquad \text{- - - (1.6)}$$

For all but the triclinic and monoclinic crystal classes, i.e. for all materials of practical interest, the principal axes of n^2 coincide with the crystal axes, so that (1.6) simplifies to

$$d_{ijk} = -n_i^2 n_j^2 r_{ijk}, \qquad \text{- - - (1.7)}$$

where the n_i are the principal refractive indices, and summation is not implied.

Theory of NLO coefficients

A widely used classical model for calculating the linear optical properties of a medium describes the electrons as harmonically bound particles. It can be extended to cover NLO effects by including anharmonic forces in the equations of motion[12]. Although only a model, the anharmonic oscillator does provide some insight into the problems of nonlinear optics, particularly into Miller's rule, the subject of the next section, where it will be discussed further.

The semi-classical theory of the interaction between radiation and matter leads to a theory of the linear optical susceptibility. Extending this method to higher order in perturbation theory leads to a description of the nonlinear interaction of several monochromatic light waves in a medium[7]. The result of this work is an explicit expression for χ_{ijk} and higher-order NLO coefficients. In the much more readable notation of Robinson[5], the result of Bloembergen and colleagues appears as

$$\chi_{ijk}^{\alpha\beta\gamma} = \frac{Ne^3}{\epsilon_o \hbar^2} \sum_{m,n} \left\{ x_{om} y_{mn} z_{no} \frac{\omega_m \omega_n + \alpha\gamma}{(\omega_m^2 - \alpha^2)(\omega_n^2 - \gamma^2)} + \right.$$

$$\left. y_{om} z_{mn} x_{no} \frac{\omega_m \omega_n + \beta\alpha}{(\omega_m^2 - \beta^2)(\omega_n^2 - \alpha^2)} + z_{om} x_{mn} y_{no} \frac{\omega_m \omega_n - \gamma\beta}{(\omega_m^2 - \gamma^2)(\omega_n^2 - \beta^2)} \right\}$$

- - - (1.8)

where each of x, y, z serves to represent any one of the Cartesian components, and $x_{om} = \langle o|x|m\rangle$. Although (1.8) is useful in exhibiting certain general properties of the coefficients, its practical value is small on account of the extreme difficulty of evaluating the matrix elements.

Robinson[5] has described an approximate method of calculating the coefficients. This variational procedure, equivalent to time-dependent perturbation theory, applies at low frequencies, i.e. well below electronic resonances, and results in an expression for χ_{ijk} in terms of ground state wave-functions only. Indeed, a detailed enough knowledge of the charge distribution is sufficient to enable useful calculations to be performed[13]. Making approximations to (1.8) in the same spirit as those leading to the Sellmeier description of linear optical properties, Robinson[5] also exhibits the close connection between the classical anharmonic oscillator model and the quantum mechanical treatments.

Miller's rule

An important and useful empirical relationship between the first-order NLO susceptibilities and the linear optical susceptibilities was discovered by Miller[14]. If the free energy function is expressed in terms of

electric polarisations rather than electric fields,

$$-F = \frac{1}{\epsilon_o^2} \underline{\underline{\underline{\Delta}}} : \underline{\underline{P}}\,\underline{P}\,\underline{P} \ , \qquad - - - (1.9)$$

then the nonvanishing elements of the tensor Δ have approximately the same value for all materials and for all effects described by (1.9), whatever their frequency. In the crystal classes with orthorhombic or higher symmetry the linear susceptibility tensor is diagonal, so that

$$\chi^{\alpha\beta\gamma}_{ijk} = \chi^{\alpha}_{ii}\,\chi^{\beta}_{jj}\,\chi^{\gamma}_{kk}\,\Delta_{ijk} \ , \qquad - - -(1.10)$$

where the χ^{α}_{ii} are the principal linear susceptibilities at frequency α. Equation (1.10) is the form originally given by Miller[14]: a more complicated relationship (see equation (2) of reference 10) obtains in the triclinic and monoclinic classes, but these do not include any crystals of practical interest.

Compilations of Miller Δ's can be found in Miller's original paper[14] and articles by Robinson[5] and Bechmann and Kurtz[10]. The latter work, concerned only with SHG coefficients, is the most recent verification of Miller's rule. The SHG d coefficients vary by four orders of magnitude ($d_{11}(Te)/d_{11}(SiO_2) \simeq 10^4$) while the Δ coefficients vary by less than one order of magnitude. The mean value of the Δ's in the tables[10] is

$\overline{\Delta}_{SHG}$ = 1.2 x 10^{-12} m V^{-1} with a standard deviation of 0.7 x 10^{-12} m V^{-1}. The LNO Δ's are more widely scattered and their mean value is slightly different from $\overline{\Delta}_{SHG}$[5]. Data on optical rectification are scarce, but also conform to Miller's rule within their generally poor experimental accuracy[5].

The physical basis of Miller's rule has been discussed extensively by Garrett and Robinson[5,15,16] and is most easily understood by reference to the anharmonic oscillator model. The frequency denominators in the expressions for the linear and nonlinear susceptibilities cancel out in the expression for Δ. This explains why Δ shows virtually no dispersion for a given material, but does not explain the relative constancy of Δ from one material to another. Since Δ is related to polarisation rather than electric field, it also normalises out local field corrections. The effect of geometry can be allowed for too: this is the main subject matter of this thesis, chapter 2 being concerned with the electro-optic effect and chapter 3 with second-harmonic generation.

The NLO bond polarisabilities calculated in chapter 3 represent, in essence, Miller Δ's with the effects of orientation and packing density removed. Their relatively small range of variation, compared with the wide range of SHG d coefficients, reflects the fact that

there are limits to the anharmonicity of the potential experienced by the electrons in a bond. Assuming that the forces involved are electrostatic, equating the harmonic and anharmonic potential energies when the displacement is of the order of the interatomic spacing gives a close estimate of $\overline{\Delta}_{SHG}$. The lower limit of Δ corresponds to a bond which is not actually homopolar. The upper limit is reached at the point where the bond becomes so asymmetric that a centrosymmetric crystal structure or local arrangement of bonds becomes energetically favoured.

The effects of ionic motion

In the last section it was remarked that Δ_{LEO} is more variable than Δ_{SHG}, and differs from it in individual materials. Quartz provides a particularly relevant example. $\Delta^{SHG}_{123} = 0$ within experimental error[14], in agreement with Kleinman's rule. On the other hand $\Delta^{LEO}_{123} \neq 0$, suggesting that Δ^{LEO} should be decomposed into an electronic and an ionic part. So far we have considered only the electronic contribution. The ionic portion arises from modulation of the linear optical susceptibility by electric-field-induced ionic motions, and is therefore related to infra-red absorption and Raman scattering[11,17].

Ionic effects can be incorporated into the oscillator model by considering anharmonic electronic and ionic oscillators with anharmonic coupling terms[16]. This vibronic oscillator model reveals the two contributions to Δ_{LaO}, and succeeds where Miller's rule fails. That is, Faust and Henry's[18] optical mixing experiments, described by (1.4), show that $\chi^{\alpha\beta\bar{\gamma}}_{ijk}$ is not proportional to χ^{α}_{ii} when α is close to the resonant frequency of an optical phonon. Garrett finds that the anharmonicity parameters are of comparable size, implying that the electronic and ionic contributions to Δ_{LaO} have the same order of magnitude. Thus although Miller's rule does not apply in the reststrahl region, it holds approximately on either side of it: $\Delta_{LaO} \simeq \Delta_{SHG}$, except in such cases as quartz.

Chapter 2

THE EFFECT OF GEOMETRY ON THE ELECTRO-OPTIC COEFFICIENTS OF OXYGEN-TETRAHEDRA COMPOUNDS

There are certain advantages to be gained from employing single crystals of cubic symmetry in light modulators using the linear electro-optic effect[19,20]. For this reason, a number of workers have investigated the double sulphate langbeinite, $K_2Mg_2(SO_4)_3$, and several of its isomorphs[21-23]. On the basis of Miller's rule[14], we expect these materials to compare quite favourably with potassium dihydrogen phosphate (KDP) and its isomorphs[24-28]: their smaller dielectric constants are partly offset by their higher refractive indices. However, such hopes are dashed by experiment: the langbeinites are distinctly inferior electro-optic materials. The explanation of this resides in the rather different geometric configurations of these two groups of crystals.

In all these materials the highly acentric and polarisable XO_4 (X = S,P,As) tetrahedra dominate the nonlinear optical behaviour. (We exclude consideration of the ammonium salts, since the NH_4^+ ion is more polarisable than the alkali metal ion it replaces, and is itself acentric, so that it can contribute

significantly to the electro-optic coefficient. Further, its orientation is usually unknown.) Because the sulphate and phosphate ions are isoelectronic, and the arsenate ion has the same complement of valence electrons, we expect their non-linear polarisabilities to be similar. Before a direct comparison can be made, we must allow for local electric fields, the number of XO_4 groups per unit volume, and their orientation.

Local fields are generally inaccessible quantities: the best way to allow for them is to compute the Miller tensor Δ[14]. This is equivalent to working in terms of electric polarisations rather than electric fields, a procedure that is more logical from the microscopic point of view. It is the polarisation of the medium, rather than the externally applied electric field, which affects the propagation of light. Various experimental results for KDP bear this out[29]. When expressed in terms of electric field, the electro-optic, piezo-electric, and elastic coefficients exhibit the same Curie-Weiss behaviour as the dielectric constant. However, when the polarisation is regarded as the appropriate variable, such temperature variation disappears, and anomalous behaviour no longer occurs at the Curie temperature.

The effect of geometry is illustrated dramatically

by considering two hypothetical cubic crystals, in which the nonlinear optical behaviour is caused solely by a tetrahedral ion. In each case there are n ions per unit volume, contributing an amount δ to the Miller tensor. In the first crystal, we imagine the bonds of all tetrahedra to be orientated in the 111, $1\bar{1}\bar{1}$, $\bar{1}1\bar{1}$ and $\bar{1}\bar{1}1$ directions. Then $\Delta = n\delta$. For the enantiomorphous crystal with bonds parallel to $\bar{1}\bar{1}\bar{1}$, $\bar{1}11$, $1\bar{1}1$ and $11\bar{1}$, $\Delta = -n\delta$. The second crystal is imagined to have an equal number of ions in each of these orientations. If these mirror-image tetrahedra are not related by the operations of the space group, the crystal will not be centrosymmetric, but Δ will certainly vanish. In real crystals the orientations generally lie between these extremes. Robinson[30], ascribing the nonlinear polarisability to the AB_4 tetrahedral units of II-VI compounds which crystallise in both the cubic zinc-blende and hexagonal wurtzite structures, has derived geometric factors for the two forms, and thence simple numerical relations between the nonlinear polarisability tensor components. We now proceed to evaluate the geometric factors (which are in the range -1 to +1) appropriate to the langbeinites and the tetragonal phosphates and arsenates.

Δ and δ are tensor quantities, so we now write

$$\Delta_{ijk} = \frac{1}{\tau}\sum_s \delta_{ijk}^{(s)} = \frac{1}{\tau}\sum_s K^{(s)} \delta'^{(s)}_{ijk} \quad , \qquad \text{- - - (2.1)}$$

where τ is the unit cell volume, the superscript s labels the XO_4 ions within the unit cell, δ is referred to the crystal axes and δ' to the tetrahedron axes. $K^{(s)}$, the geometric factor, is determined from the tensor transformation[6]

$$\delta^{(s)}_{ijk} = \sum_{pqr} a^{(s)}_{ip} a^{(s)}_{jq} a^{(s)}_{kr} \delta'^{(s)}_{pqr} \quad , \qquad \text{- - - (2.2)}$$

where the rotation matrix $\underset{\sim}{a}^{(s)}$ transforms the directions 111 etc. into the actual bond directions. Since the XO_4 ions and langbeinite have tetrahedral symmetry, and KDP has tetragonal symmetry ($\bar{4}2m$), the only non-zero components of Δ, δ and δ' have $i \neq j \neq k$. This similarity in point symmetry simplifies the calculation. We need only consider one XO_4 group: the others in the unit cell have the same geometric factor, even though their orientations are different.

The problem of finding $\underset{\sim}{a}^{(s)}$ reduces to that of choosing Cartesian axes in the tetrahedron. The vector identities

$$\left.\begin{aligned} 4(1,0,0) &\equiv (1,1,1) + (1,-1,-1) - (-1,1,-1) - (-1,-1,1), \\ 4(0,1,0) &\equiv (1,1,1) - (1,-1,-1) + (-1,1,-1) - (-1,-1,1), \\ 4(0,0,1) &\equiv (1,1,1) - (1,-1,-1) - (-1,1,-1) + (-1,-1,1), \end{aligned}\right\} \quad (2.3)$$

yield the Cartesian axes of a "standard" tetrahedron from its bond directions: from the known structures[31,32] of the crystals we can similarly derive the axes of the actual tetrahedra. The procedure is to calculate the radius vectors from the X-atom to the oxygen atoms, normalise them to $\sqrt{3}$, and add them together as prescribed in equations (2.3). The resulting vectors are normalised to unity, the normalising factors differing from 4 by a small amount depending on the departure from regularity of the tetrahedra.

The structure of KDP is depicted in figure 2.1. The tetrahedra are very nearly regular, being compressed about 1% along the z-axis. The tetrahedron's axes are found to be

$$\underline{Ox}' = (0.968,\ 0.275,\ 0),$$
$$\underline{Oy}' = (-0.275,\ 0.968,\ 0),$$
$$\underline{Oz}' = (\ 0\ ,\ 0\ ,\ 1),$$

giving

$$\underline{a}^{(s)} = \begin{pmatrix} 0.968 & -0.275 & 0 \\ 0.275 & 0.968 & 0 \\ 0 & 0 & 1 \end{pmatrix},$$

which transforms the vectors (1,1,1) etc. into the observed vectors to better than 1%. Equation (2.2)

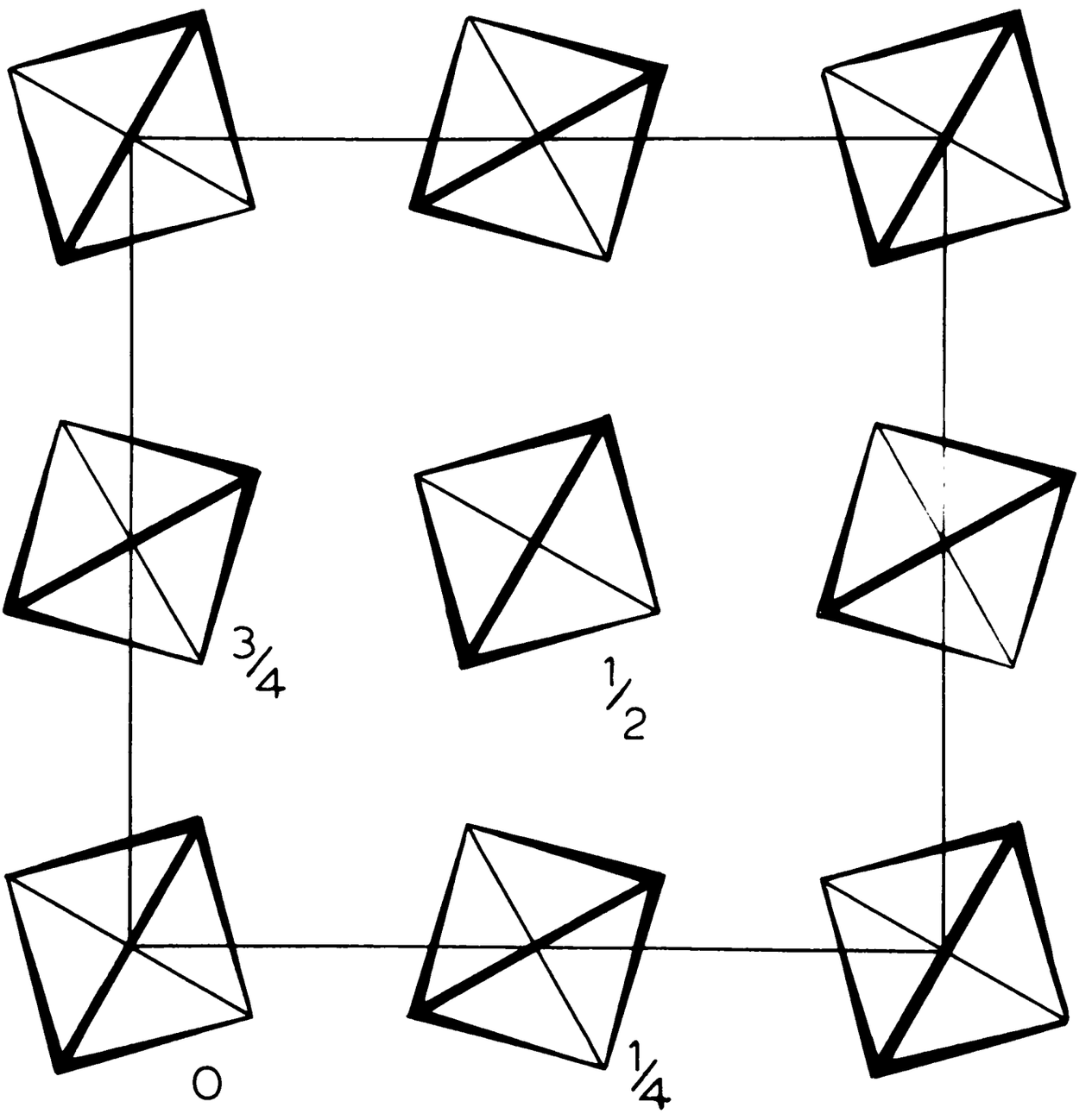


Figure 2.i Basal projection of the unit cell of potassium dihydrogen phosphate, showing the disposition of the phosphate tetrahedra and their z-coordinates.

hence yields $K^{(s)} = K = 0.86$. For potassium dihydrogen arsenate, $K = 0.84$. Atomic parameters for the other isomorphs are not available, so we assume $K = 0.85$. The structure of langbeinite is more complex. There are twelve sulphate groups in the unit cell, with twelve general orientations related by the point symmetry 23. The tetrahedra are not regular: the bond lengths have a spread of 1% about the mean value 1.48Å, and the interatomic angles differ from the tetrahedral angle 109° 28' by up to 4°. These differences are partly averaged out in the determination of the ion's axes, which are orthogonal to better than 1°. We find

$$\underset{\sim}{a}^{(s)} = \begin{pmatrix} 0.878 & -0.468 & -0.145 \\ 0.284 & 0.721 & -0.638 \\ 0.386 & 0.511 & 0.756 \end{pmatrix} ,$$

which transforms the vectors (1,1,1) etc. into the actual vectors to within 4%. Hence, for langbeinite, $K = 0.15$. Since the literature supplies only the lattice parameters of the isomorphs, we shall assume that this value applies also to them.

The results of the calculations are set out in table 2.I. The mean values of δ',

$$\delta'(SO_4^{2-}) = 3.1 \times 10^{-40},$$
$$\delta'(PO_4^{3-}) = 2.1 \times 10^{-40},$$

Table 2.I

	r_{63}	n	ϵ	d_{63}	Δ_{63}	δ' (10^{-40} m^4/V)
$K_2Mn_2(SO_4)_3$	2.0	1.62	8.4	13.8	0.71	4.0
$Rb_2Mn_2(SO_4)_3$	1.9	1.60	8.1	12.5	0.72	4.3
$Tl_2Mn_2(SO_4)_3$	2.1	1.80	14.7	22.1	0.32	1.9
$K_2Ni_2(SO_4)_3$	1.0	1.70	7.0	8.4	0.39	2.1
KH_2PO_4	10.4	1.51	21	54	1.65	1.9
KD_2PO_4	26.4	1.51	50	137	1.71	2.0
RbH_2PO_4	15.5	1.51	26	81	1.98	2.4
KH_2AsO_4	10.9	1.57	21	66	1.54	1.9
KD_2AsO_4	18.2	1.56	31	108	1.75	2.1
RbH_2AsO_4	16.0	1.56	27	95	1.77	2.3
RbD_2AsO_4	22.0	1.56	43	131	1.51	2.0

Units of r_{63}, d_{63} and Δ_{63}: 10^{-12} m/V.

$$\delta'(AsO_4^{3-}) = 2.1 \times 10^{-40},$$

are remarkably close in magnitude, when compared with a spread of a factor of 6 in Δ, and 26 in r. The larger scatter of results for the langbeinites could arise from our assumption that K = 0.15 for all isomorphs: a small change in orientation could easily alter K by 20%. Also, it is possible that the metal cations make a small contribution, but there is no systematic evidence for this. Finally, it should be noted that the standard deviations of the data in table I of reference 23 are more like 20% than the 10% errors quoted. The electro-optic coefficients of KDP and most of its isomorphs have been checked independently: the scatter of our results is comparable with the experimental accuracy.

Thus, while Miller's rule provides a good rough and ready means of predicting nonlinear optical coefficients, it is over-optimistic in cases of unfavourable geometry, and vice-versa. If structural information is available, modification of the rule to include K,

i.e. $$\chi^{\alpha\beta\gamma}_{ijk} = K \chi^{\alpha}_{ii} \chi^{\beta}_{jj} \chi^{\gamma}_{kk} \Delta_{ijk} \quad ,$$

should provide a more reliable prediction.

The work described in this chapter was carried out[33] before the importance of ionic motion, which was discussed in chapter 1, was appreciated. However, the results are

encouraging, and we have faith in them on the following grounds. We are certainly justified in considering separate XO_4 tetrahedra insofar as electronic motion is concerned. This separation assumes that distortion of the tetrahedra causes the major ionic effect. The phonons responsible, simultaneously infra-red active and Raman active, exist only in the absence of a centre of symmetry. The XO_4 tetrahedra are the most acentric constituents of the crystals concerned, and being also the most polarisable, will dominate Raman scattering. We therefore conclude that our assumption of separability is plausible.

Chapter 3

NONLINEAR OPTICAL POLARISABILITIES OF BONDS

Introduction

Several authors[34-38] have calculated nonlinear optical coefficients from various theoretical standpoints, ranging from the molecular orbital treatment of Flytzanis and Ducuing[34] to the band-theory calculations of Phillips and Van Vechten[36]. These papers have been concerned mainly with simple binary compounds (III-V, II-VI and I-VII), while Levine's bond-charge model also accounts for the NLO properties of α-quartz[37,38] and has recently been further extended[39] to cover ternary compounds (I-III-VI_2 and II-IV-V_2) with the chalcopyrite structure. No such ab initio calculations have been carried out for more complex materials, although DiDominico and Wemple[40] have related NLO coefficients to microscopic energy-band shift parameters by considering the band structure of the basic BO_6 building block common to the entire class of oxygen-octahedra ferroelectrics.

Robinson[5] has suggested that NLO effects might be describable in terms of NLO polarisabilities of individual bonds, whose effects are additive tensorially. This hypothesis is tested in this chapter, by determining

NLO bond polarisabilities empirically and thence correlating and predicting SHG coefficients in oxygen-octahedra ferroelectrics, quartz, tetragonal phosphates and arsenates and aluminium phosphate (berlinite), iodates, and sundry other materials.

As in the previous chapter, the effects of local electric fields are normalised out by means of the Miller Δ, so that, writing β for the NLO polarisability of a bond, equations (2.1) and (2.2) become

$$\Delta_{ijk} = \frac{1}{\tau}\sum_{s}\sum_{pqr} a_{ip}^{(s)} a_{jq}^{(s)} a_{kr}^{(s)} \beta_{pqr}^{(s)} \ . \qquad - - - \ (3.1)$$

A bond with cylindrical symmetry about its z-axis has two independent tensor components: $\beta_{\parallel} = \beta_{zzz}$ and $\beta_{\perp} = \beta_{xxz} = \beta_{yyz}$. The calculations of Flytzanis and Ducuing[34] show that the NLO polarisability of the bond is highly anisotropic with $\beta_{\parallel} \gg \beta_{\perp}$, so that it is a good approximation to neglect $\beta_{\perp}$. This is implicit in the charge-transfer model of Phillips and Van Vechten[36], and the bond-charge model of Levine[37,38]. Writing β_s for the sole surviving tensor component for bond s, the SHG Δ coefficients of the material are given by the simplified equations

$$\Delta_{123} = \frac{1}{\tau}\sum_{s} l_s m_s n_s \beta_s \ , \quad \Delta_{311} = \frac{1}{\tau}\sum_{s} n_s l_s^2 \beta_s \ ,$$

$$\triangle_{222} = \frac{1}{\tau}\sum_s m_s^3 \beta_s \text{ , etc.,} \qquad \text{- - - (3.2)}$$

where l_s, m_s and n_s are the direction cosines of bond s.

Clearly, $\triangle_{ijk}$ as defined above is invariant with respect to any permutation of indices. Kleinman's[9] rule would have d_{ijk} invariant, provided all the frequencies concerned are well removed from the ionic and electronic absorption regions so that dispersion can be neglected. However, under these conditions the product $\chi^{2\omega}_{ii}\chi^{\omega}_{jj}\chi^{\omega}_{kk}$ varies only slightly when the subscripts are permuted, so the small discrepancies are of no consequence. Miller[14] has suggested that it might be more appropriate to interpret Kleinman's rule in terms of $\triangle$'s rather than d's, but inspection of the tables[10] of SHG coefficients provides no conclusive evidence for either point of view.

Ferroelectric niobates

We first consider lithium niobate, $LiNbO_3$, which has three independent SHG coefficients ($d_{15} \simeq d_{31}$, d_{22} and d_{33}) allowed by crystal symmetry (3m) and Kleinman's symmetry condition. The rhombohedral unit cell[41] contains two mirror-image NbO_6 octahedra, each with three Nb-O bonds of length 1.89Å and three of 2.11Å (see figure 3.1). It has been suggested [40] that the NLO

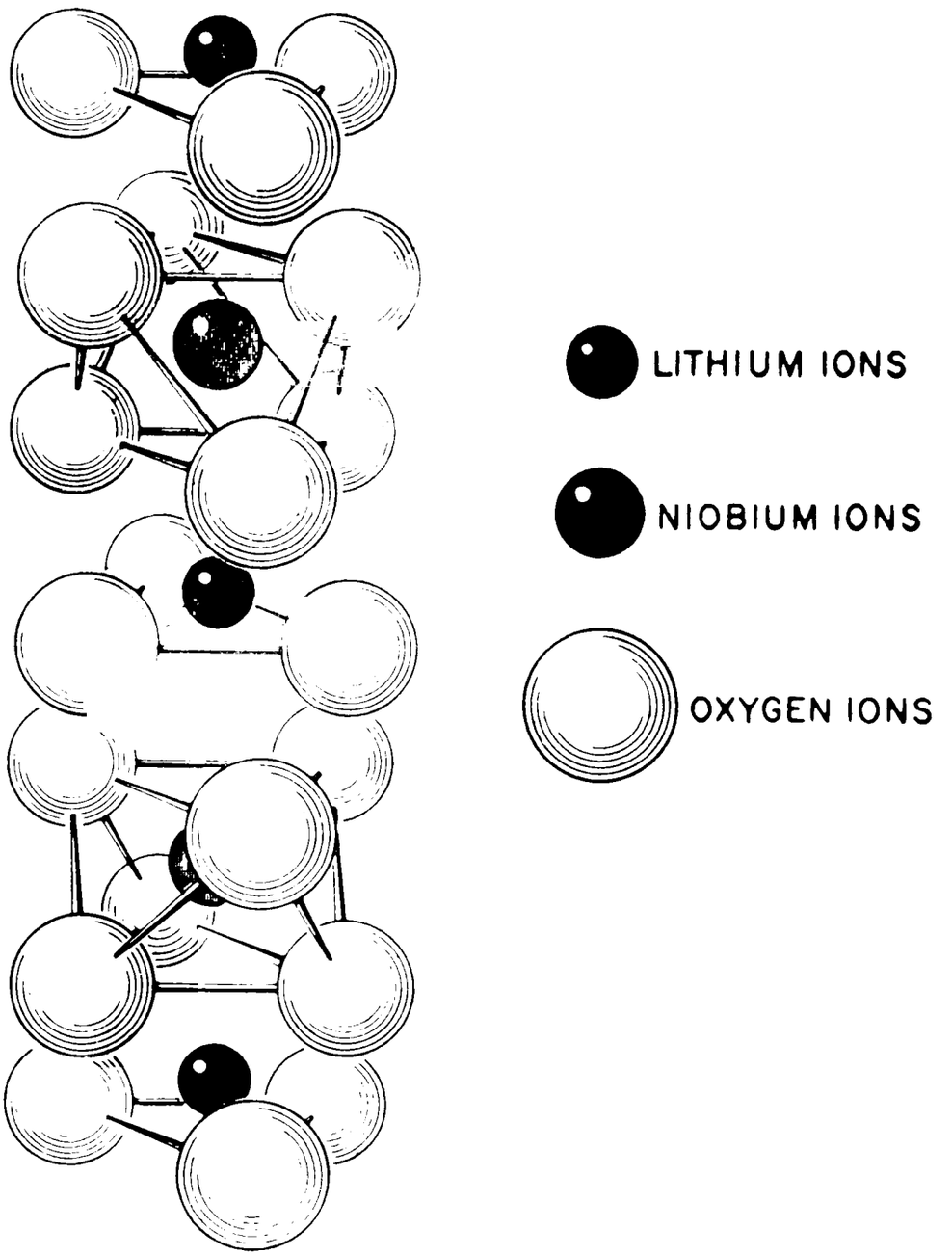


Figure 3.i The structure of lithium niobate showing two trigonally-distorted mirror-image NbO_6 octahedra.

(Reproduced from reference 40)

behaviour in niobates is dominated by the distorted NbO_6 octahedra. Consequently we suggest that NLO polarisabilities can be interpreted as residing in the Nb-O bonds themselves, which contain all the valence electrons, since the lithium atom is ionically bound and the oxygen atoms are each shared by two adjacent octahedra. NLO polarisabilities β_1 and β_2 are ascribed to the 1.89Å and 2.11Å Nb-O bonds respectively, whose direction cosines are worked out from the x-ray data[41], and equations (3.2) give

$$\Delta_{113} = \Delta_{311} = \tfrac{1}{\tau}(1.104\beta_1 - 1.106\beta_2) ,$$

$$\Delta_{222} = \tfrac{1}{\tau}(0.396\beta_1 - 0.195\beta_2) , \qquad \text{- - - (3.3)}$$

$$\Delta_{333} = \tfrac{1}{\tau}(0.643\beta_1 - 1.796\beta_2) .$$

The β's are overdetermined and we therefore have a check on our assumptions that $\beta_\perp$ is negligible and that the Nb-O bond electrons are the only important ones. From the refractive index data and the measured SHG coefficients[10,42,43] d_{31} and d_{22}, we compute the β's and thence $d_{33} = -(55 \pm 8)d_K$, in reasonable agreement with the measured[10] $d_{33} = (86 \pm 22)d_K$. ($d_K = |d_{36}(KH_2PO_4)|$.)

When this work was originally carried out[44], the only available sign information was that d_{31} and d_{22}

have opposite sign[45], so we arbitrarily took d_{31} to be positive. Since then, Miller and Nordland[46,47] have measured the absolute signs of SHG coefficients in a number of important materials including $LiNbO_3$, and found that d_{31} is negative. Our results now carry absolute signs, which are therefore opposite to those in reference 44.

The calculation above shows that d_{33} is negative, allowing us to compute β's giving a best fit to all three equations (3.3):

$$\beta_1 = +(76 \pm 10)10^{-30} m^3 d_K \text{ and } \beta_2 = +(98 \pm 13)10^{-30} m^3 d_K .$$

The errors are derived from the experimental uncertainties in the d coefficients using standard procedures[48]. The two β's are comparable in magnitude and have the same sign, which is expected since the bond directions were uniformly chosen to point from niobium to oxygen. The d's corresponding to these values are given as theory in table 3.I; their agreement with the experimental values[10] is good enough to support our simplifying assumptions and give us confidence that predictions for other niobates will not be too far wrong.

Before we can proceed to other niobates, we must postulate some dependence of β on bond length, r. Levine[49] has found that $\beta \propto r^n$, where n is a function

of ionicity and $n \simeq 7$ for compounds of the type AB and less for more ionic compounds. It is unnecessary to know the exact dependence, since the range of variation of r is small, and any smooth monotonic function of r will give essentially similar results. The Nb-O bond is largely covalent in character[50,51], so we assume $\beta = Ar^7 + B$. From the $LiNbO_3$ data, $\beta = (0.218r^7 + 57.3)10^{-30}m^3d_K$ when r is expressed in Å. Almost identical β's and SHG coefficients were predicted when a linear dependence was assumed.

Potassium lithium niobate[52] ($K_3Li_2Nb_5O_{15}$) and barium strontium niobate[53] ($Ba_{0.27}Sr_{0.75}Nb_2O_{5.78}$) have very similar tetragonal (4mm) tungsten-bronze-type structures (figure 3.ii). Barium sodium niobate[54] ($Ba_2NaNb_5O_{15}$) has a slightly distorted form of this structure with orthorhombic (mm2) symmetry: its a- and b-axes are $\sqrt{2}$ times longer than the a-axes of its tetragonal pseudo-cell, and rotated through 45° from them. Tables 3.II to 3.IV show, for each type of bond, the length of the bond, the sum of the products of direction cosines, and the NLO polarisability. Equations (3.2) then give the SHG coefficients, which are displayed as theory in table 3.I. The numerical agreement with experiment[55-57] is fair, in view of the assumptions made. The sign predictions which have since

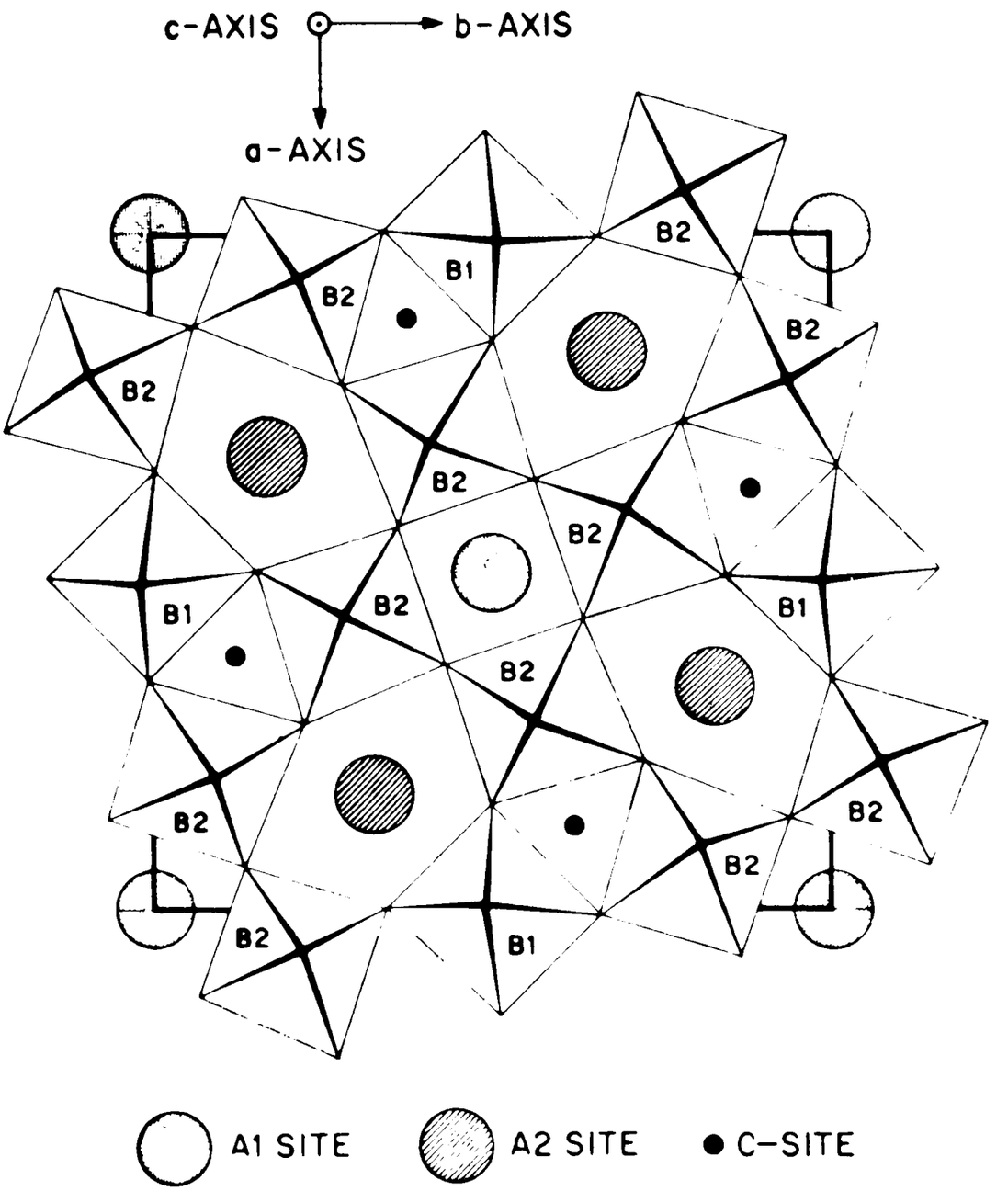


Figure 3.ii Tetragonally-distorted tungsten-bronze-type structure of barium strontium niobate and potassium lithium niobate. The site occupancies are:

	A1	A2	B1	B2	C
$Ba_{0.27}Sr_{0.75}Nb_2O_{5.78}$	Sr	Ba/Sr	Nb	Nb	-
$K_3Li_2Nb_5O_{15}$	K	K	Nb	Nb	Li

(Reproduced from reference 40)

Table 3.I

Calculated and measured SHG coefficients of niobates, relative to d_K.

		Theory	Experiment
$LiNbO_3$	d_{15}	-15 ± 4	- 12.3± 1.8
	d_{31}	-15 ± 4	- 12.3± 1.8
	d_{22}	+ 7.3± 2.8	+ 6.5± 0.6
	d_{33}	-63 ±14	(-)86 ±22
$K_3Li_2Nb_5O_{15}$	d_{15}	-12 ± 2	13 ± 3
	d_{31}	-11 ± 2	15 ± 3
	d_{33}	-16 ±11	27 ± 3
$Ba_{0.27}Sr_{0.75}Nb_2O_{5.78}$	d_{15}	- 5.5± 2.2	-
	d_{31}	- 5.5± 2.2	-
	d_{33}	-16 ± 5	-
$Ba_2NaNb_5O_{15}$	d_{15}	-17 ± 4	(-)28 ± 3
	d_{31}	-16 ± 4	(-)27 ± 5
	d_{24}	-20 ± 4	(-)29 ± 3
	d_{32}	-19 ± 4	(-)32 ± 3
	d_{33}	-34 ± 8	(-)32 ± 3

been verified experimentally[47] are shown in parentheses in table 3.I. The SHG coefficients of barium strontium niobate have not been reported in the literature: experimental comparison would be of interest.

The approach presented here uses approximations established for the sp^3 hybrid tetrahedral bond. The results show that they can reasonably be applied to the octahedral bond, which has a significant amount of d character. Since this model considers electronic motion only, neglecting ionic motion, it does not apply to electro-optic effects. Indeed, it is found that the linear electro-optic coefficients of $LiNbO_3$ are all positive[58], confirming the importance of ionic effects[17].

Tables 3.II to 3.IV:

For bond nomenclature see references 52 to 54.

The unit of β is $10^{-30} m^3 d_K$.

Table 3.II

Details of $K_3Li_2Nb_5O_{15}$

Bond type	Length(Å)	$\sum n_i l_i^2$	$\sum n_i^3$	β_i
Nb(1) - O(1)	1.938	-0.372	-0.007	80
Nb(1) - O(4)	2.130	0	+2	101
Nb(1) - $O(4)_z$	1.885	0	-2	76
Nb(2) - O(1)	1.972	-0.361	-0.006	83
Nb(2) - O(2)	1.942	-0.267	-0.002	80
Nb(2) - $O(2)_i$	1.998	-0.263	-0.002	85
Nb(2) - O(3)	1.996	-0.267	-0.002	85
Nb(2) - O(5)	1.847	+0.007	+7.976	73
Nb(2) - $O(5)_z$	2.171	-0.005	-8.000	107

Table 3.III

Details of $Ba_{0.27}Sr_{0.75}Nb_2O_{5.78}$

Bond type	Length(Å)	$\sum n_i l_i^2$	$\sum n_i^3$	β_i
Nb(1) - O(1)	1.951	-0.611	-0.031	81
Nb(1) - O(4a)	1.92	+0.020	+1.941	78
Nb(1) - $O(4a)_z$	2.03	-0.018	-1.944	88
Nb(2) - O(1)	1.949	-0.503	-0.017	80
Nb(2) - $O(2)_i$	1.958	+0.452	+0.012	81
Nb(2) - $O(2)_{vi_x}$	2.013	+0.440	+0.011	86
Nb(2) - O(3)	2.004	-0.344	-0.005	86
Nb(2) - $O(5a)_i$	1.88	+0.082	+3.748	75
Nb(2) - $O(5b)_i$	1.93	+0.017	+3.951	80
Nb(2) - $O(5a)_{i_z}$	2.11	-0.066	-3.806	97
Nb(2) - $O(5b)_{i_z}$	2.00	-0.016	-3.953	84

Table 3.IV

Details of $Ba_2NaNb_5O_{15}$

Bond type	Length(Å)	$\sum n_i l_i^2$	$\sum n_i m_i^2$	$\sum n_i^3$	β_i
Nb(1) - O(1)	1.976	-0.474	-0.548	-0.018	83
Nb(1) - O(9)	1.765	+0.049	0	+1.925	69
Nb(1) - $O(9)_z$	2.270	-0.030	0	-1.956	125
Nb(2) - O(6)	1.977	-0.518	-0.427	-0.014	83
Nb(2) - O(10)	1.835	+0.021	0	+1.967	73
Nb(2) - $O(10)_z$	2.179	-0.015	0	-1.978	108
Nb(3) - O(1)	1.941	-0.850	-0.055	-0.012	80
Nb(3) - O(2)	2.006	-0.065	-0.697	-0.007	86
Nb(3) - O(4)	1.988	-0.078	-0.678	-0.007	84
Nb(3) - O(5)	1.935	-0.981	-0.110	-0.021	80
Nb(3) - O(7a)	1.837	+0.077	+0.009	+3.870	73
Nb(3) - O(7b)	1.885	+0.105	+0.003	+3.835	76
Nb(3) - $O(7a)_z$	2.196	-0.054	-0.007	-3.910	110
Nb(3) - $O(7b)_z$	2.159	-0.080	-0.002	-3.876	105
Nb(4) - O(3)	2.009	+0.443	+0.048	+0.002	86
Nb(4) - O(4)	1.947	-0.094	-0.711	-0.008	81
Nb(4) - O(5)	2.012	-0.951	-0.129	-0.021	86
Nb(4) - O(6)	1.955	-0.050	-0.875	-0.013	81
Nb(4) - O(8a)	1.854	+0.002	+0.062	+3.899	74
Nb(4) - O(8b)	1.815	+0.016	+0.069	+3.878	71
Nb(4) - $O(8a)_z$	2.169	-0.002	-0.045	-3.923	107
Nb(4) - $O(8b)_z$	2.216	-0.010	-0.046	-3.913	114

Lithium tantalate

Ferroelectric $LiTaO_3$ is isomorphous with $LiNbO_3$[59,60]. However, there are small but significant differences in atomic positions between the two materials, resulting in a TaO_6 octahedron which is more nearly regular than the NbO_6 one. The lower Curie temperature and spontaneous polarisation of $LiTaO_3$ are fundamentally related to the smaller displacement of the Ta atom from its central position in the nonpolar phase[61]. On our bond polarisability model, this smaller distortion also accounts for the smaller SHG coefficients[10,43].

From the structural data[59,60], we compute

$$\Delta_{113} = \Delta_{311} = \frac{1}{\tau}(1.131\beta_1 - 1.129\beta_2) ,$$

$$\Delta_{222} = \frac{1}{\tau}(0.410\beta_1 - 0.261\beta_2) , \qquad - - - (3.4)$$

$$\Delta_{333} = \frac{1}{\tau}(0.782\beta_1 - 1.624\beta_2) .$$

These equations are very similar to the corresponding equations (3.3) for $LiNbO_3$, so it is not surprising that the same choice of relative signs must be made in order to achieve a consistent solution. The best fit values

$$\beta_1 = +(81 \pm 8)10^{-30}m^3d_K \text{ and } \beta_2 = +(88 \pm 9)10^{-30}m^3d_K$$

give the SHG coefficients (relative to d_K) shown overleaf.

Since the original calculations were performed[44], the relative signs have been verified and the absolute signs measured experimentally[46,47]. These are shown in the table.

Coefficient	Calculated	Measured
d_{15}	-3.3 ± 0.8	-2.7 ± 0.5
d_{31}	-3.3 ± 0.8	-2.7 ± 0.5
d_{22}	$+4.9 \pm 1.9$	$+4.4 \pm 0.5$
d_{33}	-37 ± 7	-41 ± 5

Barium titanate

Ferroelectric $BaTiO_3$ has the tetragonally distorted perovskite structure[62] depicted in figure 3.iii. The titanium atoms are displaced upwards, and the oxygen atoms downwards, from their symmetric positions at the body- and face-centres, respectively. There are three types of Ti-O bond; $Ti\text{-}O_{11}$, $Ti\text{-}O_{12}$ and $Ti\text{-}O_{2x}$. The structural data give

$$\Delta_{113} = \frac{1}{\tau}(-0.109\beta_2) ,$$

and $$\Delta_{333} = \frac{1}{\tau}(-\beta_{11} + \beta_{12} - 0.0006\beta_2) ,$$

for the two independent SHG coefficients allowed by

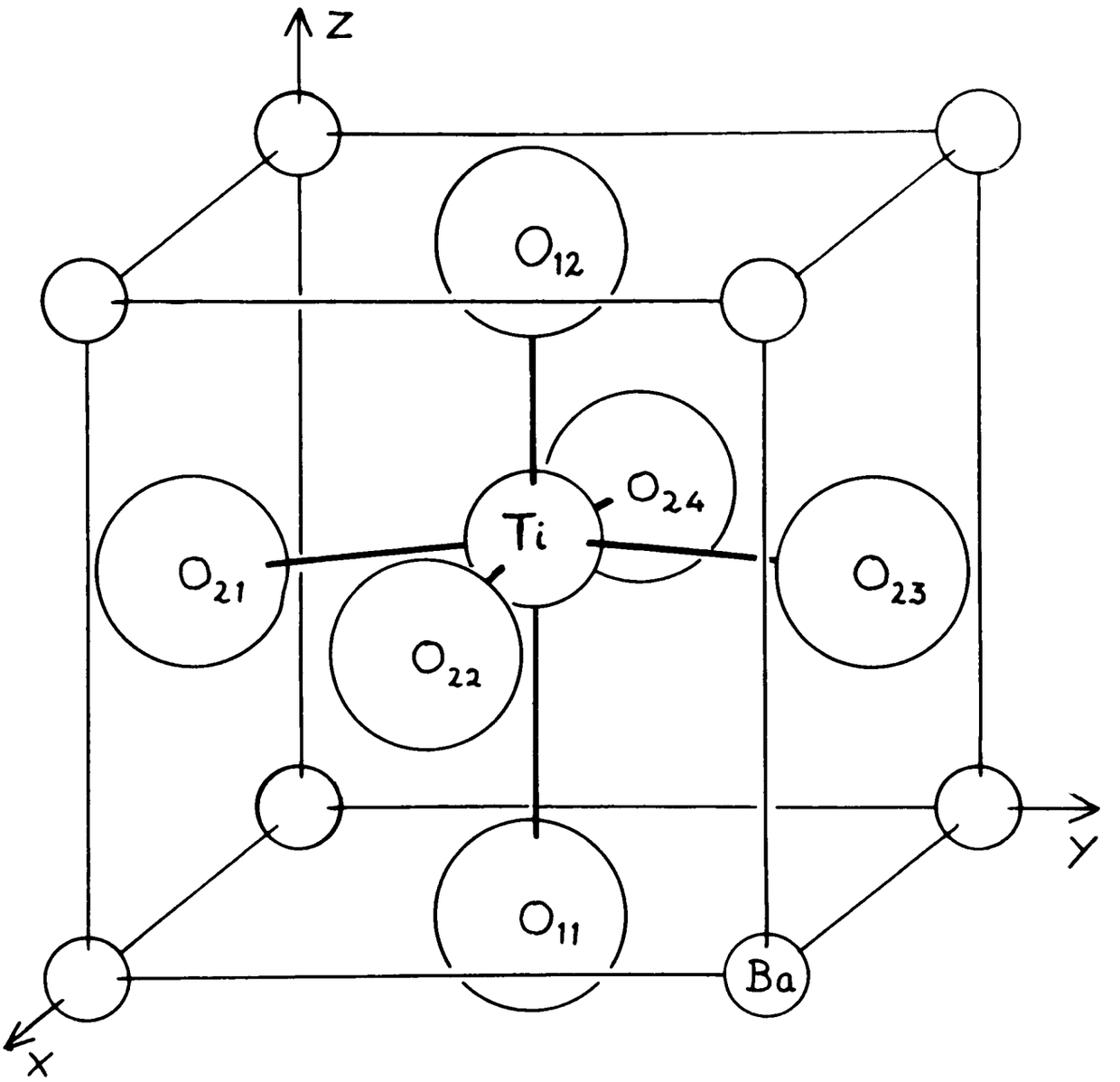


Figure 3.iii The unit cell of barium titanate.

crystal symmetry and Kleinman's rule. Substituting the experimental SHG coefficients[10,63,64,47] into these equations gives

$$\beta_{11} - \beta_{12} = +(10.1 \pm 0.7)10^{-30}m^3d_K ,$$

$$\beta_2 = +(227 \pm 19)10^{-30}m^3d_K .$$

β_{11} and β_{12} can be determined if we assume, as before, that $\beta = Ar^7 + B$, since this reduces the number of unknown quantities from three to two. We thus obtain the values below for the NLO polarisability of the Ti-O bond.

Bond	Length (Å)	$\beta\,(10^{-30}m^3d_K)$
$Ti - O_{11}$	2.170	$\beta_{11} = +233 \pm 19$
$Ti - O_{12}$	1.864	$\beta_{12} = +223 \pm 19$
$Ti - O_{2x}$	2.000	$\beta_2 = +227 \pm 19$

α-Quartz

Ordinary low-temperature quartz belongs to the enantiomorphous point group 32, which allows SHG coefficients d_{11} and d_{14}. Kleinman's rule predicts $d_{14} = 0$, as does our model. The structure of the laevo-rotatory crystal is described by Wyckoff[65]. In the hexagonal unit cell there are three very nearly regular SiO_4 tetrahedra, with Si-O = 1.61Å. One NLO polarisability is therefore required, and is related to the macroscopic SHG coefficient by

$$\Delta_{111} = \frac{1}{\tau}(0.968\beta).$$

Experimentally[57,47], $d_{11} = +(0.77 \pm 0.04)d_K$,

whence $$\beta = +(35 \pm 2)10^{-30}m^3 d_K .$$

Tetragonal phosphates and arsenates

Potassium dihydrogen phosphate (KDP) and its isomorphs have already been encountered in chapter 2. There are sixteen equivalent P-O (or As-O) bonds per unit cell, and one independent SHG coefficient ($d_{14} \simeq d_{36}$) allowed by crystal symmetry ($\bar{4}2m$) and Kleinman's rule. Thus

$$\Delta_{123} = \frac{16}{\tau} lmn\beta .$$

Table 3.V contains the numerical values to be substituted into this equation, and the values of β derived. Nordland[66] has recently found that d_{14} and d_{36} for KDP are positive. Our theory predicts the same sign for these coefficients in all the phosphates, and it is almost certain that it also applies to the arsenates. The values of Δ (relative to d_K) are mean values derived from d_{14} and d_{36} given in the SHG tables[10], except for CDA ($Cs\ H_2AsO_4$) and RDA (RbH_2AsO_4), whose Δ-coefficients are given by Suvorov et al.[67], without refractive index data. Because of lack of structural information, τ and lmn have been estimated for some materials: the errors involved are negligible (one or two per cent).

The NLO polarisabilities calculated for the P-O bond agree within experimental error. The weighted mean value is

$$\beta_{P-O} = (83.5 \pm 2.5)10^{-30} m^3 d_K .$$

For the As-O bond the agreement is poorer. This is probably due to experimental error. The SHG coefficients of CDA and RDA have been measured only by Suvorov et al.[67], who obtain a value for KDA some 30% lower than that obtained by other workers[14,12,11]. Making allowance for this, the As-O bond probably has an NLO polarisability

$$\beta_{As-O} = (50 \pm 10)10^{-30} m^3 d_K .$$

Table 3.V

Tetragonal phosphates and arsenates

	Δ_{123}	$\tau(\text{Å}^3)$	161mn	β $(10^{-30} m^3 d_K)$
$(NH_4)H_2PO_4$	0.58 ± 0.06	426	2.68	89 ± 9
$(ND_4)D_2PO_4$	0.62 ± 0.10	424	2.68	95 ±15
KH_2PO_4	0.55 ± 0.02	388	2.62	82 ± 3
KD_2PO_4	0.55 ± 0.06	388	2.62	82 ± 8
RbH_2PO_4	0.59 ± 0.09	418	2.65	93 ±15
CsH_2AsO_4	0.17 ± 0.03	501	2.55	34 ± 5
KH_2AsO_4	0.35 ± 0.05	417	2.55	57 ± 9
RbH_2AsO_4	0.23 ± 0.03	448	2.55	40 ± 6

Aluminium phosphate (berlinite)

The polymorphic structures of aluminium phosphate and silicon dioxide are very similar. However, $AlPO_4$ seems to be much more ionic than SiO_2. If $AlPO_4$ were predominantly covalent, one might expect Al and P to replace Si in a random manner, whereas all forms are found to be ordered[68]. The P-O bond lengths of 1.51 to 1.52Å in berlinite (corresponding to ∝-quartz) and 1.54Å in a form closely resembling low-cristobalite agree well with the bond lengths in phosphates recognised as ionic. Dietzel and Poegel[69] found that "it was impossible to produce an amorphous glass by cooling $AlPO_4$ which melted at 2000°C; the product was always crystalline. $AlPO_4$ seems to behave as an ionic compound with PO_4 complex anions and there is therefore no possibility of forming a glass."

The structure of berlinite has been accurately determined by Schwarzenbach[70], who finds that the relationship of the optical activity to the absolute configuration is the same as in quartz. His Fourier difference synthesis shows that the electron density is much greater between P and O than between Al and O, implying that the structure consists of covalently bonded PO_4^{3-} ions and Al^{3+} ions.

We therefore neglect the Al-O bonds, and treat $AlPO_4$ as we treated KDP and isomorphs, considering only the P-O bonds. It is found that

$$\Delta_{111} = \frac{1}{\tau}(1.06\beta).$$

Inserting the experimental SHG coefficient[10,14] gives

$$\beta = (85 \pm 7)10^{-30}m^3d_K ,$$

which provides two-fold confirmation that $AlPO_4$ is ionic. Firstly, this value of β agrees remarkably well with that found for the tetragonal phosphates (83.5 ± 2.5). Secondly, if $AlPO_4$ were covalent like quartz, we would expect our calculation to yield a value of β twice that of the Si-O bond, because we have neglected half the bonds - the Al-O bonds. $2\beta_{Si-O} = (70 \pm 4)10^{-30}m^3d_K$, which does not agree with our result.

Alpha-iodic acid and lithium iodate

The large polarisability of the IO_3 group, and its acentricity due to the non-bonded pair of electrons, suggested iodates as useful new nonlinear optical materials[71]. The technique of measuring SHG in powders[72] showed that several iodates had phase-matchable SHG coefficients larger than that of quartz, leading to

subsequent studies on single crystals of α-HIO_3[73,74] and $LiIO_3$[75,76]. The measurements of $d_{31}(LiIO_3) = d_{31}^L$ by Nash et al. (NBBT)[75] and by Nath and Haussühl (NH)[76] differ by a factor of three. By using the bond polarisability model to compare the SHG coefficients of $LiIO_3$ and α-HIO_3 it can be shown that the value obtained by NBBT is the more reliable one.

The crystal structure of $LiIO_3$ has been elucidated recently[77,78]. The unit cell contains two trigonally distorted IO_6 octahedra. Each iodine atom is surrounded by three oxygen atoms at a distance of 1.81Å, forming what may be regarded as a trigonal pyramidal IO_3 group, and a further three oxygen atoms, each belonging to a different IO_3 group, at a distance of 2.88Å. Thus there are two NLO polarisabilities to be related to the two independent SHG coefficients ($d_{15} \simeq d_{31}$, d_{33}) allowed by crystal symmetry (6) and Kleinman's symmetry condition.

Iodic acid likewise contains discrete IO_3 anions[79,80], disposed about the unit cell in much the same way as the ClO_3 and BrO_3 groups in cubic $NaClO_3$ and $NaBrO_3$, which will be discussed later. However, HIO_3 is orthorhombic, and the IO_3 pyramids are not regular, having I-O separations of 1.78, 1.82 and 1.90Å. As in $LiIO_3$, there are also three longer, weaker bonds with lengths 2.51, 2.77 and 2.88Å. Crystal symmetry (222) and Kleinman's

rule allow one independent SHG coefficient ($d_{14} \simeq d_{25} \simeq d_{36}$).

Ascribing an average NLO bond polarisability β_1 to the short I-O bond, and β_2 to the long bond, we obtain

$$\Delta^{L}_{311} = \frac{1}{\tau^{L}}(1.107\beta_1 - 1.152\beta_2) , \qquad - - - (3.5)$$

$$\Delta^{L}_{333} = \frac{1}{\tau^{L}}(0.656\beta_1 - 1.267\beta_2) , \qquad - - - (3.6)$$

$$\Delta^{H}_{123} = \frac{1}{\tau^{H}}(-1.169\beta_1 + 1.384\beta_2) , \qquad - - - (3.7)$$

where the superscripts L and H denote $LiIO_3$ and HIO_3 respectively. Eliminating β_1 and β_2 from these equations gives

$$\Delta^{H}_{123} = -0.47\Delta^{L}_{311} - 0.15\Delta^{L}_{333} . \qquad - - - (3.8)$$

NBBT find that $\left| d^{L}_{33}/d^{L}_{31} \right| = 0.8 \pm 30\%$ whence

$$\left| \Delta^{L}_{333}/\Delta^{L}_{311} \right| = 1.27 \pm 0.38,$$

and $\Delta^{H}_{123} = (-0.66 \pm 0.06)\Delta^{L}_{311}$ if $d^{L}_{33}/d^{L}_{31} > 0$,

or $\Delta^{H}_{123} = (-0.28 \pm 0.06)\Delta^{L}_{311}$ if $d^{L}_{33}/d^{L}_{31} < 0$.

Substituting the experimental values[75,76] for $LiIO_3$ into these expressions gives the results shown in table 3.VI, where the measured value of Δ^{H}_{123}[73,74] is included. Good agreement is found in the two cases marked (i) and (ii) in table 3.VI, but comparison of the corresponding β's with values found for other types of bond (see table 3.VII) shows quite clearly that (i) is the correct

Table 3.VI

	d_{33}^L/d_{31}^L	Δ_{123}^H (relative to d_K; signs relative to d_{31}^L)	
NBBT	Positive	-0.59 ± 0.10	(i)
	Negative	-0.24 ± 0.06	
NH	Positive	-1.65 ± 0.21	
	Negative	-0.68 ± 0.10	(ii)
Experimental		0.63 ± 0.10 (sign unknown)	

Table 3.VII

Bond	β ($10^{-30} m^3 d_K$) (short bond)		(long bond)
Nb - O	$+ 76 \pm 10$		$+ 98 \pm 13$
Ta - O	$+ 81 \pm 8$		$+ 88 \pm 9$
Ti - O	$+ 223 \pm 19$		$+ 233 \pm 19$
Si - O		$+ 35 \pm 2$	
P - O		84 ± 3	
As - O		50 ± 10	
I - O (i)	36 ± 80		137 ± 80
I - O (ii)	1410 ± 250		1060 ± 240

choice since it gives β's of the same order of magnitude as in other materials, whereas (ii) gives anomalously large values.

The results of NBBT are thus confirmed, and the relative signs of all the coefficients predicted for the particular enantiomorphs studied[78,79]. If d_{31}^{L} is positive, then d_{33}^{L} is positive and d_{14}^{H} is negative. Since these results were obtained[81], the relative signs in $LiIO_3$ have been confirmed by Jerphagnon[82] using the Maker fringe technique. He finds $d_{31}^{L} = (11.9 \pm 1.0)d_K$ and $d_{33}^{L} = (12.4 \pm 1.0)d_K$, in good agreement with NBBT. Campillo and Tang[83], measuring spontaneous parametric scattering, also find that $d_{31}^{L} \simeq 12d_K$.

The absolute signs of the coefficients in $LiIO_3$ have been measured[47], but we cannot determine the signs of the β's because the absolute configuration of the structure has not been established. The two structure determinations[77,78] describe opposite enantiomorphs, but since the sense of the z-axis is the same in each, they describe a mirror pair, rather than an inversion pair, so that the SHG tensor elements do not change sign. The piezoelectric constants likewise remain unchanged, so that defining the positive sense of the z-axis to be such that the piezoelectric coefficient d_{33} is positive

makes the distinction between enantiomorphs trivial for our purposes. This is the procedure adopted by Miller and Nordland[47], and is more useful in the present circumstances than the convention[84] of making d_{33} positive for the right crystal and negative for the left crystal. Thus, to find the signs of the β's, we need to know whether the z-axis of the unit cell corresponds to the positive or negative z-axis as defined by Miller and Nordland, and no consideration need be given to the enantiomorphism.

Sodium chlorate and bromate

These isomorphous materials belong to the enantiomorphous point group 23, and therefore have one independent SHG coefficient d_{14}. Their structures[85,86] are discussed fully in chapter 4, where the relationship between SHG and optical activity is investigated. Here we are concerned with estimating their NLO bond polarisabilities.

As in the iodates, there are discrete pyramidal XO_3 ions (X = Cl,Br) with bond lengths Cl-O = 1.49Å, Br-O = 1.66Å, and three longer (~3Å) weaker X-O bonds. Ascribing NLO polarisabilities β_1 and β_2 respectively to these bonds, we find

$$\Delta_{123} = \frac{1}{\tau}(-0.151\beta_1 - 0.011\beta_2) \text{ for dextro-NaClO}_3 ,$$

$$\Delta_{123} = \frac{1}{\tau}(-0.154\beta_1 - 0.003\beta_2) \text{ for laevo-NaBrO}_3 .$$

The unfavourable geometric factor for the long bond allowes us to neglect its effect initially. β_1 and β_2 are of the same order of magnitude, and even if $\beta_2 \simeq 4\beta_1$ as for $LiIO_3$, this procedure overestimates β_1 by only 30% in $NaClO_3$, and 8% in $NaBrO_3$. Thus, from the measured SHG coefficients[87,57,47] we find

$$\beta_1(\text{Cl-O}) = -(70 \pm 14)10^{-30}\text{m}^3\text{d}_K ,$$

$$\beta_1(\text{Br-O}) = +(15 \pm 3)10^{-30}\text{m}^3\text{d}_K .$$

If we now make some allowance for β_2, assuming $\beta_2 = (3 \pm 2)\beta_1$, we estimate

$$\beta_1(\text{Cl-O}) = -(60 \pm 20)10^{-30}\text{m}^3\text{d}_K ,$$

$$\beta_1(\text{Br-O}) = +(14 \pm 4)10^{-30}\text{m}^3\text{d}_K .$$

Zinc oxide

Zincite, ZnO, crystallises with the tetrahedrally-coordinated hexagonal wurtzite structure. The point group symmetry (6mm) allows three independent SHG coefficients, which have been measured by Miller[10,14]; $d_{15} = +(4.9 \pm 0.4)d_K$; $d_{31} = +(4.4 \pm 0.4)d_K$; $d_{33} = -(14.8 \pm 0.4)d_K$. Kleinman's rule predicts $d_{31} \simeq d_{15}$, which is seen to be true here. The signs of the coefficients have been measured recently by Miller and Nordland[88,46], who also remeasured the ratio $\left|d_{33}/d_{31}\right| = (3.0 \pm 0.3)$, in agreement with the earlier determination[10,14]: (3.2 ± 0.4).

This ratio is important theoretically. Assuming the ZnO_4 (or OZn_4) tetrahedra to be regular, Robinson[30] and Levine[37] predict $d_{33}/d_{31} = -2$, while we predict $\Delta_{333}/\Delta_{311} = -2$, whence $d_{33}/d_{31} = -2.08$ using Bond's[89] refractive index data. Phillips and Van Vechten[36], averaging a third-order moment over the four tetrahedral bonds, arrive at a factor -22/9, but their method of doing so is not made clear, and they quote wrong direction cosines for the bonds.

The structure has been reinvestigated recently and the absolute configuration determined[90]. There is one Zn-O bond of length 1.99Å along the c-axis, and three of length 1.97Å making angles of 108° with the c-axis and

111° with each other. We find that $\Sigma n_i^3 = 1.821$ and $\Sigma n_i l_i^2 = -0.840$, whence $\Delta_{333}/\Delta_{311} = -2.17$ and $d_{33}/d_{31} = -2.28$. This is an insignificant improvement, and the value of $\beta_{\parallel}$ which best fits the experimental data, $\beta_{\parallel} = -13.6 \times 10^{-30} m^3 d_K$, gives $d_{33} = -13.5 d_K$, $d_{31} = d_{15} = 6.0 d_K$. These numbers differ from the experimentals values by up to four standard deviations, and are unsatisfactory.

We fare no better if we retain $\beta_{\perp}$, which we have neglected up to now. For regular tetrahedra

$$\Delta_{311} = \frac{8}{9\tau}(\beta_{\parallel} - 3\beta_{\perp}),$$

$$\Delta_{333} = +\frac{16}{9\tau}(\beta_{\parallel} - 3\beta_{\perp}).$$

For the actual bonds, the coefficients of $\beta_{\perp}$ are different, but still close to three, so that although a solution of the equations is possible, it is ill-determined and worthless. Since the bonding orbitals are almost pure sp^3 hybrid, and therefore the symmetry of the bonds is very nearly cylindrical, further contributions to equation (3.1) need not be considered.

So far we have assumed that all the bonds are identical. According to the crystallographic evidence they are quite similar. Further, in the wurtzite-type crystals ZnS[91], CdS[63,10,91] and CdSe[91], $\left|d_{33}/d_{31}\right| = 2$

within the experimental uncertainties, supporting this assumption. However, 6mm is a polar point group, permitting the existence of an internal field parallel to the c-axis. Robinson[5] has shown that $d_{33}/d_{31} = -2$ only when this field is negligible: when it is dominant, the expected ratio is +3, and in intermediate cases any value is possible. Jerphagnon[92] arrives at the same conclusions via group theory, and also derives the empirical relationship

$$2\Delta_{311} + \Delta_{333} = CP_s ,$$

where C is a constant and P_s is the spontaneous polarisation. Thus, looking at the whole group of wurtzite-type crystals, we see that the effect of the internal field is negligible in ZnS, CdS, and CdSe; is small in ZnO; and dominates in BeO, for which $d_{33}/d_{31} = +1.4$[93]. Unfortunately, Jerphagnon and Newkirk's[93] point-charge calculation of P_s is wrong[94], because their tetrahedral units cannot be built up into a real crystal. It turns out that P_s is nonzero even when the tetrahedra are regular. The order of magnitude of P_s then follows from the fact that the real charges are much smaller than the formal charges[95], rather than from the small departure from exact tetrahedral symmetry.

Thus we take the two types of bond to be different. The internal field will affect their first-order NLO polarisabilities differently via the next-order non-linearity. Ascribing β_1 to the c-axis bonds and β_2 to the others, we have

$$\Delta_{311} = \frac{1}{\tau}(-0.840\beta_2),$$

$$\Delta_{333} = \frac{1}{\tau}(2\beta_1 - 0.179\beta_2),$$

whose solution is

$$\beta_1 = -(14.5 \pm 0.4)10^{-30}m^3d_K$$

and $$\beta_2 = -(10.5 \pm 0.9)10^{-30}m^3d_K.$$

Summary and discussion

In this chapter we have calculated NLO bond polarisabilities from experimentally determined SHG coefficients. These empirical quantities can then be used to predict SHG coefficients of new materials with known structures, as was done for niobates and, in effect, for HIO_3 and $AlPO_4$.

The compounds chosen comprise most of those which contain X-O bonds and whose SHG coefficients have been measured. This large group contains many materials that are widely used in the visible region.

Unfortunately, it is not really large enough to allow one to discern trends, especially as the various elements X are scattered over the periodic table. The only closely related group consists of chlorates, bromates and iodates, for which $\beta(Cl\text{-}O) = -(60 \pm 20)$, $\beta(Br\text{-}O) = +(14 \pm 4)$ and $\beta(I\text{-}O) = (36 \pm 80)10^{-30} m^3 d_K$ for the shorter bond. From these figures it is reasonable to conclude that the I-O bond has a positive β.

Phillips and Van Vechten[36] have related NLO susceptibilities to electronegativity over a wide range of binary compounds with the zinc-blende and wurtzite structures. For the more diverse and complex structures we have considered, no such simple relationship exists, as can be seen in table 3.VIII where we compare the β of the X-O bond with the electronegativity difference $(x_O - x_X)$ on Pauling's[95] scale. Of course the electronic structure of a bond depends not only on the two atoms at its ends, but also on the other bonds made by these atoms. Accordingly, the coordination numbers of the X and oxygen atoms are also included in the table.

Scrutiny of the table reveals that β increases with electronegativity difference for the same

Table 3.VIII

NLO bond polarisabilities, electronegativity differences, and coordination numbers of the X and O atoms for various X-O bonds.

Bond	β ($10^{-30} m^3 d_K$)	Electronegativity difference	Coordination number of X atom	Coordination number of O atom
Nb-O	+ 87 ± 12	1.9	6	2
Ta-O	+ 85 ± 9	2.0	6	2
Ti-O	+228 ± 20	2.0	6	2
Si-O	+ 35 ± 2	1.7	4	2
P-O	84 ± 3	1.4	4	1
As-O	50 ± 10	1.5	4	1
I-O	36 ± 80	1.0	6	2
Cl-O	- 60 ± 20	0.5	6	2
Br-O	+ 14 ± 4	0.7	6	2
Zn-O	- 13 ± 3	1.9	4	4

coordination arrangement. This is to be expected since the electronegativity difference is a measure of bond acentricity: the more electronegative atom (oxygen) will exert a greater pull on the bond electrons.

Also, β increases with "coordination ratio", defined as

$$C.R. = \frac{\text{Number of O atoms around an X atom}}{\text{Number of X atoms around an O atom}} .$$

This fits in with the above arguments. The greater the number of oxygen atoms surrounding an X atom, the smaller the pull exerted by the X atom on the electrons in each bond. Or, conversely, if there are fewer X atoms around an oxygen atom, its electronegative effect will be enhanced.

It is interesting to observe that these trends can be combined: β varies quite smoothly with the product of electronegativity difference and coordination ratio, as shown in figure 3.iv. The one really exceptional point is for the Ti-O bond. This anomalously large nonlinear polarisability is almost certainly connected with the extremely large linear polarisability (rutile has a mean refractive index of 2.7), and the explanation of both probably resides in the proximity of the 4s and 3d energy levels in the first transition group. The easy admixture of s and d states will allow large

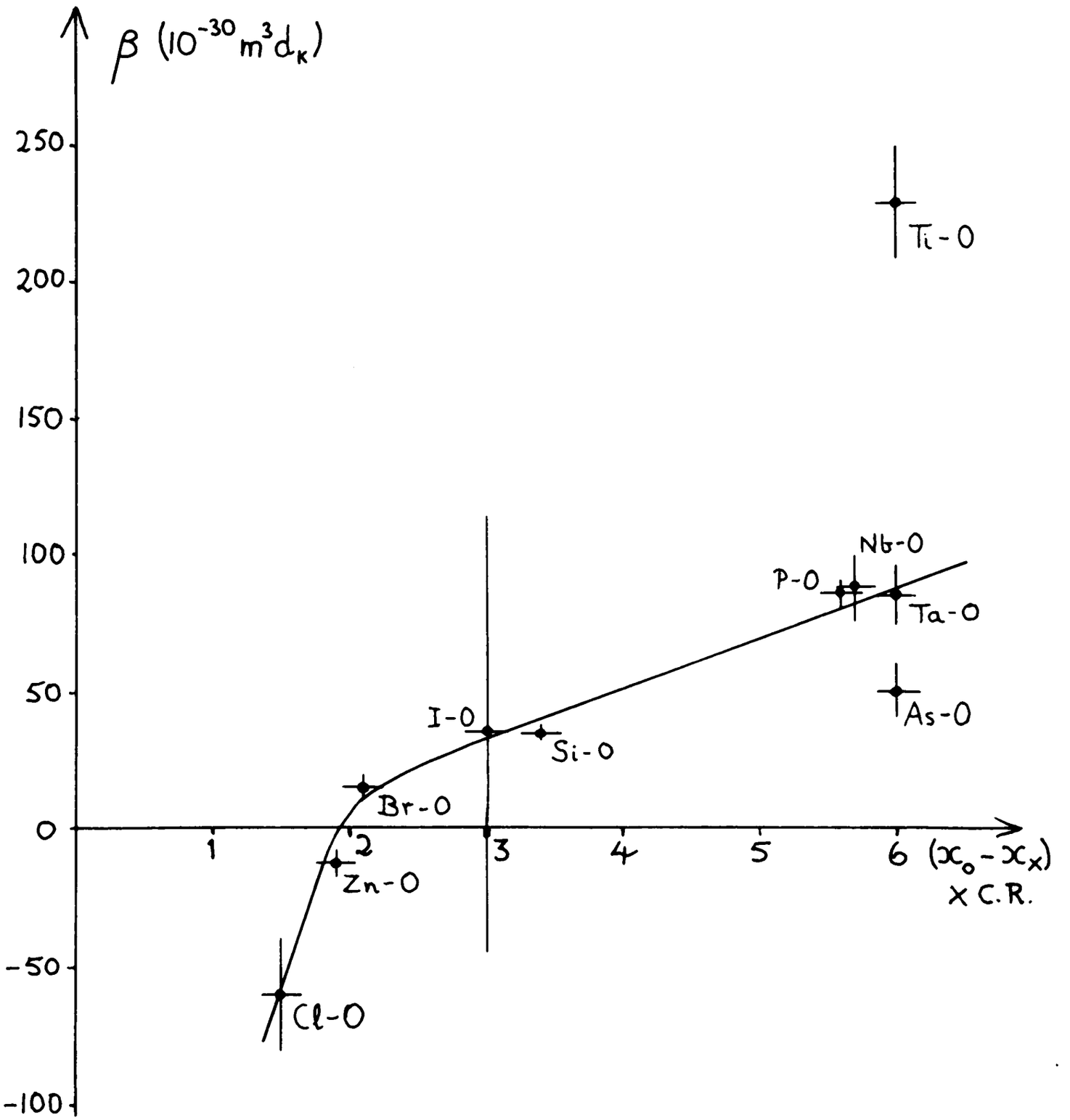


Figure 3.iv Plot of NLO bond polarisability against electronegativity difference ($x_O - x_X$) times coordination ratio (C.R.).

electric dipole moment matrix elements for the transitions responsible for optical susceptibilities.

The reason for the particular dependence of β on electronegativity difference and coordination ratio is obscure. In diatomic molecules the bond dipole moment is roughly proportional to electronegativity difference[95]. Crude point charge models of bonding suggest that in more complicated molecules and crystals the dipole moment depends also on coordination, but not necessarily in a simple way. β can be expressed as a cubic moment of the electronic distribution[5]: again using simple point charge models, we can thence express β as a cubic polynomial in electric dipole moment. One could draw together these tenuous threads of argument and persuade oneself that they supply an explanation, but on the whole it seems better to regard the curve of figure 3.iv as empirical. This being so, it is hoped to study further materials in order to plot more points on the graph, and so make a better assessment of its value as a predictive tool.

Chapter 4

OPTICAL ACTIVITY AND NONLINEAR OPTICS

Symmetry considerations

The fundamental physical cause of optical activity is the change of phase of the electromagnetic vectors of a light wave over the length of a molecule or crystal unit cell. This may be expressed by the phenomenological constitutive equations[96]

$$\frac{1}{\epsilon_0}D_i = \epsilon_{ij}E_j + \alpha_{ijk}\frac{\partial}{\partial x_j}E_k \,, \qquad \text{- - - (4.1)}$$

$$\frac{1}{\mu_0}B_i = \mu_{ij}H_j + \beta_{ijk}\frac{\partial}{\partial x_j}H_k \,. \qquad \text{- - - (4.2)}$$

We shall consider the tensor α_{ijk}: the treatment of β_{ijk} is exactly analogous. The law of conservation of energy requires that $\epsilon_{ij} = \epsilon_{ji}$ and $\alpha_{ijk} = -\alpha_{kji}$, so that we may write

$$\alpha_{ijk} = e_{ilk}\alpha_{lj} \,, \qquad \text{- - - (4.3)}$$

where e_{ilk} is the completely anti-symmetric unit tensor of rank three, and α_{lj} is an arbitrary second-rank pseudo-tensor. (4.1) now becomes

$$\frac{1}{\epsilon_0}\underline{D} = \underline{\underline{\epsilon}}\cdot\underline{E} + (\underline{\underline{\alpha}}\cdot\underline{\nabla})\wedge\underline{E} \,. \qquad \text{- - - (4.4)}$$

For plane harmonic waves, we may write $\underline{\nabla} = ink\underline{s}$, where

n is the refractive index, $k = \omega/c$ is the wave-number in vacuo, and $\underline{s}$ is the unit wave normal. Thus

$$\frac{1}{\epsilon_o}\underline{D} = \underline{\underline{\epsilon}}\cdot\underline{E} + ink(\underline{\underline{\alpha}}\cdot\underline{s})\wedge\underline{E} \qquad - - - (4.5)$$

which is identical to the more familiar description of Born[97];

$$\frac{1}{\epsilon_o}\underline{D} = \underline{\underline{\epsilon}}\cdot\underline{E} + i\underline{G}\wedge\underline{E} ,$$

where $\underline{G}$ is the gyration vector. Substituting equation (4.5) into the wave-equation, it is found[97,98] that the refractive indices and the ratios of the components of $\underline{D}$ are independent of the antisymmetric part of α_{ij}, so that this tensor may be chosen in a symmetric form for the purpose of determining n and the optical rotatory power. In an isotropic medium, α_{ij} reduces to the pseudo-scalar α, and (4.4) becomes

$$\underline{D} = \epsilon_o\epsilon\underline{E} + \epsilon_o\alpha\underline{\nabla}\wedge\underline{E} . \qquad - - - (4.6)$$

Using Faraday's law of electromagnetic induction, we have

$$\underline{D} = \epsilon_o\epsilon\underline{E} - g\dot{\underline{H}} , \qquad - - - (4.7)$$

the constitutive relation used by Condon[99,100]. This expression in terms of magnetic field is far more useful in calculations than the basic formulation in terms of field gradients (4.1).

Thus optical activity may be described by an antisymmetric third-rank tensor or a symmetric second-rank pseudo-tensor. The latter is easier to handle, and Nye[6] tabulates its form for the crystal point groups. The effect vanishes in the centrosymmetric classes, and exists in fifteen of the twenty-one acentric classes.

In liquids, the symmetry restrictions are the same for optical activity and sum- and difference-frequency generation[101], both effects being described by antisymmetric third-rank tensors. Writing the nonlinear polarisation in the form

$$\begin{aligned}\frac{1}{\epsilon_0}P_i &= \chi^{\alpha\beta\gamma}_{ijk}E^{\beta}_{j}E^{\gamma}_{k} \\ &= \tfrac{1}{4}(\chi^{\alpha\beta\gamma}_{ijk} + \chi^{\alpha\beta\gamma}_{ikj})(E^{\beta}_{j}E^{\gamma}_{k} + E^{\beta}_{k}E^{\gamma}_{j}) \\ &\quad + \tfrac{1}{4}(\chi^{\alpha\beta\gamma}_{ijk} - \chi^{\alpha\beta\gamma}_{ikj})(E^{\beta}_{j}E^{\gamma}_{k} - E^{\beta}_{k}E^{\gamma}_{j}) \\ &= \tfrac{1}{2}S^{\alpha\beta\gamma}_{ijk}(E^{\beta}_{j}E^{\gamma}_{k} + E^{\beta}_{k}E^{\gamma}_{j}) + \tfrac{1}{2}A^{\alpha\beta\gamma}_{ijk}(E^{\beta}_{j}E^{\gamma}_{k} - E^{\beta}_{k}E^{\gamma}_{j}) \quad , \end{aligned} \tag{4.8}$$

we see that $\chi^{\alpha\beta\gamma}_{ijk}$ may be decomposed into a symmetric part $S^{\alpha\beta\gamma}_{ijk} = S^{\alpha\beta\gamma}_{ikj}$, and an antisymmetric part $A^{\alpha\beta\gamma}_{ijk} = -A^{\alpha\beta\gamma}_{ikj}$. In acentric isotropic media (point group $\infty\infty$), S vanishes, leaving A to account for first-order optical nonlinearities with $\alpha \neq \beta \neq \gamma$. (Clearly $A^{\alpha\beta\gamma}_{ijk} = -A^{\alpha\beta\gamma}_{ikj} = -A^{\alpha\gamma\beta}_{ijk} = 0$ when $\beta = \gamma$, since we may always interchange subscripts and frequencies simultaneously, so that second-harmonic generation is impossible in liquids.) Giordmaine et

al.[101-103] have studied optical activity and sum-frequency generation in liquids, and their correlation, both experimentally and theoretically. However, no such investigation has been carried out for crystals, despite the interesting result of Simon and Bloembergen[87], that crystals of sodium chlorate and sodium bromate with identical structures have SHG coefficients and optical rotatory powers of opposite sign.

SHG is described by the tensor S, so that the s symmetry restrictions on SHG and optical activity in crystals are not identical, but they are sufficiently close to suggest a correlation. Each effect is electronic, and each has been described in terms of an anharmonic oscillator model[12,99]. In this chapter it is shown that the model of reference 99 gives a rough quantitative account of both phenomena in sodium chlorate and bromate crystals.

The change of sign of third-rank tensors under inversion can be observed directly in enantiomorphous media. The sum-frequency intensity is the same for d- and l-arabinose solutions, but vanishes in a racemic mixture[102]. Simon and Bloembergen's second-harmonic interference experiments also demonstrate this for d- and l-$NaClO_3$ crystals.

The anharmonic oscillator model of Condon, Altar and Eyring[99]

The normal polarisation modes of an optically active medium are left- and right-circularly polarised, with different refractive indices n_l and n_r. A plane-polarised wave will suffer a rotation of its plane of polarisation through angle $\phi = (n_l - n_r)\pi/\lambda$ per unit length (λ is the vacuum wavelength). Substituting the phenomenological constitutive relations

$$\begin{aligned} \underline{D} &= \epsilon_o \epsilon \underline{E} - g\dot{\underline{H}} , \\ \underline{B} &= \mu_o \underline{H} + g\dot{\underline{E}} , \end{aligned} \qquad \text{- - - (4.9)}$$

into Maxwell's equations leads to

$$n_l = \sqrt{\epsilon} + \omega c g , \quad n_r = \sqrt{\epsilon} - \omega c g , \qquad \text{- - -(4.10)}$$

and $$\phi = \omega^2 g. \qquad \text{- - -(4.11)}$$

The microscopic analogues of equation (4.9) are

$$\begin{aligned} \underline{p}_i &= \alpha \underline{E}' - \mu_o \beta \dot{\underline{H}} , \\ \underline{m}_i &= \beta \dot{\underline{E}}' , \end{aligned} \qquad \text{- - -(4.12)}$$

where $\underline{p}_i$ and $\underline{m}_i$ are the induced electric and magnetic dipole moments of a bond, and $\underline{E}'$ is the local electric field ($\underline{H}' = \underline{H} = \underline{B}/\mu_o$ at optical frequencies). In the description of the linear optical effect of optical

activity there is no analogue of the Miller Δ which allows for local field effects in nonlinear optical phenomena. However, we will be dealing only with cubic crystals, so that consistent use of Lorentz local field corrections should not lead us far astray. Thus

$$(n^2-1)/(n^2+2) = N\alpha/3\epsilon_0, \quad g = \tfrac{1}{3}(n^2+2)N\mu_0\beta , \quad ---(4.13)$$

and

$$\phi = \tfrac{1}{3}\omega^2(n^2+2)N\mu_0\beta , \quad ---(4.14)$$

where N is the number of bonds per unit volume.

Rosenfeld's extension of the quantum theory of dispersion to include β has been reviewed by Condon[100]. The final result, valid for cubic crystals as well as isotropic media, is

$$\alpha = \frac{2}{3\hbar}\sum_n \frac{\omega_n |\langle o|\hat{\underline{p}}|n\rangle|^2}{\omega_n^2-\omega^2} , \quad ---(4.15)$$

$$\beta = \frac{2}{3\hbar}\sum_n \frac{\mathrm{Im}\left(\langle o|\hat{\underline{p}}|n\rangle . \langle n|\hat{\underline{m}}|o\rangle\right)}{\omega_n^2-\omega^2} , \quad ---(4.16)$$

for a system in its electronic ground state. Here $\hat{\underline{p}}$ and $\hat{\underline{m}}$ are the electric and magnetic dipole moment operators, and $\hbar\omega_n = (E_n - E_o)$ is the excitation energy of state n. β vanishes if the bond has a centre of symmetry, since $\langle o|\hat{\underline{p}}|n\rangle$ is a vector whereas $\langle n|\hat{\underline{m}}|o\rangle$ is a pseudo-vector. β also vanishes if the bond has a symmetry plane: $\langle o|\hat{\underline{p}}|n\rangle$ must lie in the plane while

$\langle n|\hat{\underline{m}}|o\rangle$ must be perpendicular to it.

In Condon's[99] model, a valence electron moves in the potential

$$V = \tfrac{1}{2}m(\omega_x^2x^2 + \omega_y^2y^2 + \omega_z^2z^2) + Axyz \ . \qquad - - - (4.17)$$

The anharmonic term destroys the central symmetry of a harmonic oscillator, and the anisotropy removes all mirror planes. (If, for example, $\omega_x = \omega_y$, the potential is symmetric about the planes $x = \pm y$.) The small anharmonic term is neglected in calculating the linear response, so that

$$\alpha = (e^2/3m)\left\{1/(\omega_x^2 - \omega^2) + 1/(\omega_y^2 - \omega^2) + 1/(\omega_z^2 - \omega^2)\right\} ,$$

leading to a Sellmeier-type dispersion formula[104]

$$n^2 - 1 = \sum_i \frac{A_i \lambda_i^2}{\lambda^2 - \lambda_i^2} \ . \qquad - - - (4.18)$$

To work out β, the matrix elements in (4.16) are evaluated using first-order perturbation theory. The result is

$$\beta = \frac{A\hbar e^2}{12m^3}\left\{F(\omega_x, \omega_y, \omega_z, \omega) + F(\omega_y, \omega_z, \omega_x, \omega) + F(\omega_z, \omega_x, \omega_y, \omega)\right\} \qquad - - -(4.19a)$$

where

$$F(\omega_x,\omega_y,\omega_z,\omega) = \left(\frac{1}{\omega_y}-\frac{1}{\omega_z}\right)\frac{1}{(\omega_y+\omega_z)^2-\omega_x^2}\left(-\frac{1}{\omega_x^2-\omega^2}+\frac{1}{(\omega_y+\omega_z)^2-\omega^2}\right)$$

(equation 33 of reference 99)

$$= \left(\frac{1}{\omega_z}-\frac{1}{\omega_y}\right)\left(\frac{1}{(\omega_y+\omega_z)^2-\omega^2}\right)\left(\frac{1}{\omega_x^2-\omega^2}\right) \quad \text{- - -(4.19b)}$$

The expression (1.8) for the SHG coefficient can be evaluated exactly for the potential (4.17), again using first-order perturbation theory to evaluate the matrix elements. The result of a long and tedious calculation is

$$\chi_{xyz}^{\alpha\beta\gamma} = -\frac{ANe^3}{2m^3\epsilon_0}\frac{1}{(\omega_x^2-\alpha^2)(\omega_y^2-\beta^2)(\omega_z^2-\gamma^2)}, \qquad \text{- - - (4.20)}$$

identical to the result of a completely classical calculation. Several authors[101,7,16] have commented on this property of the oscillator, without explanation.

Application to $NaClO_3$ and $NaBrO_3$

In (4.20) we have tacitly assumed that all N bonds per unit volume have their axes parallel to the crystal axes (x,y,z). In $NaClO_3$ and $NaBrO_3$ the twelve halogen-oxygen bonds per unit cell have twelve general orientations equivalent under the operations of the crystal point group, 23. We now compute the geometric factor for this arrangement.

We rewrite (4.20) for SHG in a single bond, referred to Cartesian axes (x',y',z') appropriate to the bond:

$$\delta^{2\omega\,\omega\,\omega}_{x'y'z'} = -\frac{Ne^3}{2m^3\epsilon_0}\,\frac{1}{(\omega_x^2-4\omega^2)(\omega_y^2-\omega^2)(\omega_z^2-\omega^2)}\,. \qquad ---\ (4.21)$$

Inspection of (4.17) shows that the bond has orthorhombic (222) symmetry, allowing the tensor elements δ_{14}, δ_{25} and δ_{36}. The bond axes are related to the unit cell axes by twelve rotation matrices $\underset{\sim}{a}^r$: $\underline{x} = \underset{\sim}{a}^r\underline{x}'$. Thus the one independent SHG coefficient of these cubic crystals is

$$\chi^{2\omega\,\omega\,\omega}_{123} = \frac{1}{\tau}\sum_r\sum_{ijk} a^r_{1i}a^r_{2j}a^r_{3k}\delta_{ijk}$$

$$= \frac{1}{\tau}\sum_r\Big\{a^r_{11}(a^r_{22}a^r_{33} + a^r_{23}a^r_{32})\delta_{14} + a^r_{12}(a^r_{23}a^r_{31} + a^r_{21}a^r_{33})\delta_{25} + a^r_{13}(a^r_{21}a^r_{32} + a^r_{22}a^r_{31})\delta_{36}\Big\}\,,$$

where τ is the unit cell volume. Now $\underset{\sim}{a}^r = \underset{\sim}{r}\underset{\sim}{a}$, where $\underset{\sim}{r}$ is one of the twelve rotation matrices representing point group 23, and $\underset{\sim}{a}$ defines the orientation of one particular bond. By this means the sum over r is readily evaluated, giving

$$\chi^{2\omega\,\omega\,\omega}_{123} = \frac{C}{\tau}(\delta_{14} + \delta_{25} + \delta_{36})\,, \qquad ---\ (4.22)$$

with $$C = 4\Big\{a_{11}(a_{22}a_{33} + a_{23}a_{32}) + a_{12}(a_{23}a_{31} + a_{21}a_{33}) + a_{13}(a_{21}a_{32} + a_{22}a_{31})\Big\}\,. \qquad ---\ (4.23)$$

The experimental SHG coefficient is given by

$$d_{14}^{2\omega} = \tfrac{1}{2}\left(\frac{n_\omega^2+2}{3}\right)^2\left(\frac{n_{2\omega}^2+2}{3}\right)\chi_{123}^{2\omega\,\omega\,\omega}$$

where we have again used a Lorentz local field correction factor, and the factor of one half arises from the difference between the experimental and theoretical representations of time-varying fields. Thus

$$d_{14}^{2\omega} = \left(\frac{n_\omega^2+2}{3}\right)^2\left(\frac{n_{2\omega}^2+2}{3}\right)\frac{c}{2\tau}(\delta_{14}+\delta_{25}+\delta_{36}),$$

$$\delta_{14} = -\frac{Ae^3}{2m^3\epsilon_0}\frac{1}{(\omega_x^2-4\omega^2)(\omega_y^2-\omega^2)(\omega_z^2-\omega^2)} \quad . \qquad -\,-\,(4.24)$$

Using the technique of anomalous x-ray scattering, Ramachandran and Chandrasekaran[105] have shown that the parameters of Zachariasen[106] for $NaClO_3$, when referred to right-handed axes, describe the dextro-rotatory form. Aravindakshan[85] has since re-determined the structure, and we use his more accurate parameters. Bijvoet and co-workers[86] have similarly determined the absolute configuration of $NaBrO_3$, and find that the same structure (structure A) describes the laevo-rotatory form. The space group of these crystals is $P2_13$ (T^4), with the sodium and halogen atoms in the special positions (4a) and the oxygen atoms in the general positions (12b) (Wyckoff notation). The close similarity of the structures can be seen by inspecting the parameters in table 4.I. The unit cell of d-$NaClO_3$ is depicted in

figure 4.1.

Table 4.I

Parameters of $NaClO_3$ and $NaBrO_3$

	$NaClO_3$ (Aravindakshan)	$NaBrO_3$ (Bijvoet et al.)
Lattice parameter (Å)	6.570	6.705
x_{Na}	0.066	0.077
$x_{Halogen}$	0.418	0.406
x_O	0.307	0.287
y_O	0.594	0.597
z_O	0.508	0.508

The ClO_3^- ion has the form of a regular trigonal pyramid, with the chlorine atom at the apex (see figure 4.11). Initially, we make the usual assumption that the bond has cylindrical symmetry, and choose the z'-axis in the direction Cl → O. The other two oxygen atoms in the ion reduce this symmetry, giving the bond a mirror plane normal to the base of the pyramid. We choose the x'-axis perpendicular to this plane, and the y'-axis to complete an orthogonal right-handed set.

From the x-ray data, taking

Cl_1 at (2.746, 2.746, 2.746) (Å)

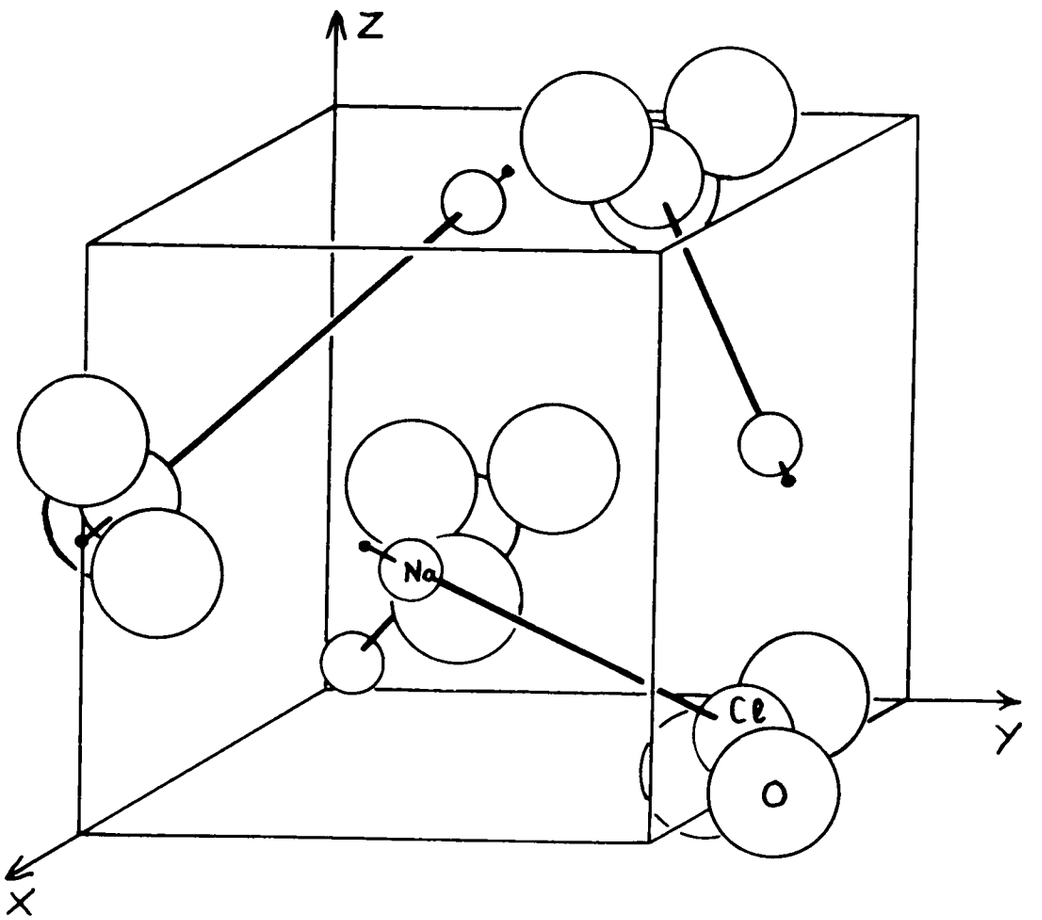


Figure 4.i Crystal structure A of dextro-rotatory $NaClO_3$ and laevo-rotatory $NaBrO_3$.

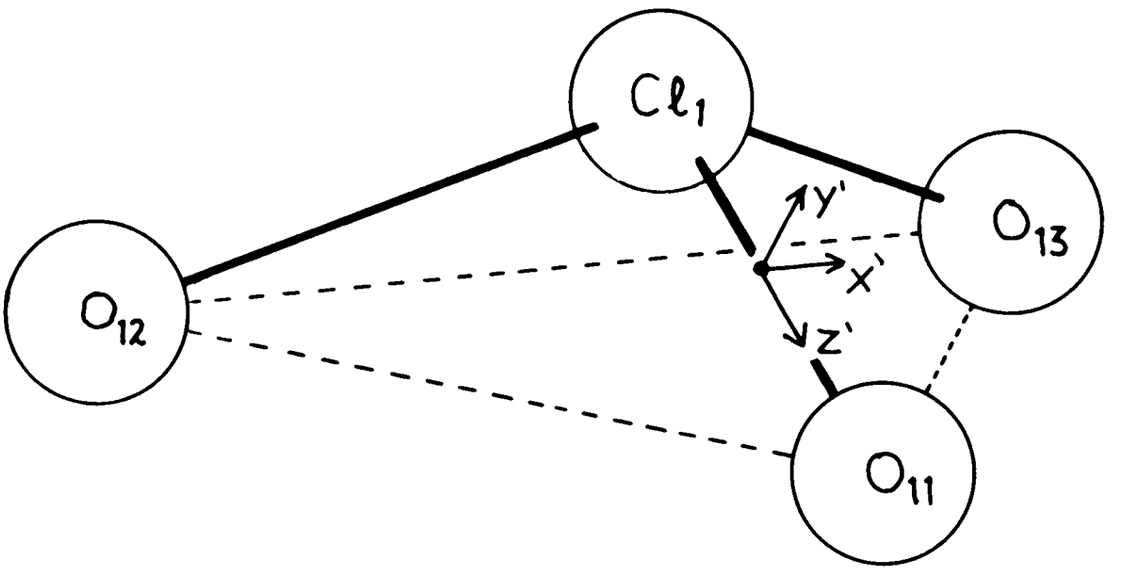


Figure 4.ii The chlorate ion in sodium chlorate.

O_{11} at (2.017, 3.903, 3.338),

O_{12} at (3.338, 2.017, 3.903),

O_{13} at (3.903, 3.338, 2.017),

we find for the bond $Cl_1 - O_{11}$ that

$\underline{Oz}'$ = (-0.489, 0.776, 0.397), Cl-O = 1.49Å.

$\underline{Ox}'$ is in the direction $O_{12} \rightarrow O_{13}$, whence

$\underline{Ox}'$ = (0.238, 0.557, -0.766), O-O = 2.37Å.

$\underline{Oy}' = \underline{Oz}' \wedge \underline{Ox}'$ = (-0.839, -0.295, -0.458).

Hence $$\underset{\sim}{a} = \begin{pmatrix} 0.238 & -0.839 & -0.489 \\ 0.557 & -0.295 & 0.776 \\ -0.796 & -0.458 & 0.397 \end{pmatrix}$$

and $C = 0.92.$

Similarly, for $NaBrO_3$,

$$\underset{\sim}{a} = \begin{pmatrix} 0.228 & -0.846 & -0.482 \\ 0.565 & -0.288 & 0.773 \\ -0.793 & -0.448 & 0.413 \end{pmatrix}$$

and $C = 0.91.$

The values of the frequencies ω_x, ω_y and ω_z are next considered. Of these, ω_z will be least since it

corresponds to oscillation along the Cl-O bond. ω_x and ω_y will be roughly comparable, with $\omega_y > \omega_x$. This follows from the well-known fact that the lone-pair - bonded-pair repulsion is greater than bonded-pair - bonded-pair repulsion ($\widehat{LClO} = 113^o$; $\widehat{OClO} = 105^o$; L = lone pair). Motion in the y'-direction (see figure 4.ii) will be impeded on one side by the repulsion of the chlorine atom lone pair, and on the other by the other two Cl-O bonds in the ion. Motion in the x'-direction is impeded only by one Cl-O bond on each side.

The magnitudes of the frequencies must be determined indirectly since the U.V. spectra of $NaClO_3$ and $NaBrO_3$ crystals are not to be found in the literature. Chandrasekhar and Madhava[107] have measured the refractive and optical rotatory dispersion in these media, and expressed them by formulae using the same characteristic wavelengths. For $NaClO_3$ they find λ_i = 185 and 90 nm, corresponding to ω_i = 1.0 and 2.1 x 10^{16} rad.s^{-1}, and for $NaBrO_3$, λ_i = 200 and 90 nm, ω_i = 0.95 and 2.1 x 10^{16} rad.s^{-1}. We assign these values to ω_z and ω_x respectively. ω_y can only be obtained from an informed guess, so that order-of-magnitude agreement is all that can be claimed for the final result. Because molecular energy levels generally become closer together towards higher energy, we expect ω_y to be fairly close to ω_x and ω_z. At the

same time, it must be far enough removed from them to permit the use of a two-term Sellmeier formula, which is known to be accurate[107]. This separation, however, need not be large.

The quantal expression for the linear susceptibility is

$$\chi_{xx} = \frac{2Ne^2}{\epsilon_0 h^2} \sum \frac{\omega_n x_{on} x_{no}}{\omega_n^2 - \omega^2} \quad .$$

The matrix elements x_{on} decrease rapidly as the energy, $\hbar\omega_n$, of state $|n\rangle$ increases. Thus refractive dispersion can be accurately accounted for by a one- or two-term Sellmeier formula, with characteristic frequencies close to the first, or first two, absorption frequencies.

These considerations restrict ω_y to the region around 3×10^{16} rad.s^{-1}. Substituting $\omega_x = 2.1 \times 10^{16}$, $\omega_y = 3.0 \times 10^{16}$ and $\omega_z = 1.0 \times 10^{16}$ into equations (4.14) and (4.19), together with the linear optical data quoted by Simon and Bloembergen[87], we obtain $A = -8 \times 10^{12}$ J m^{-3}. Taking $\omega_y = 2.5 \times 10^{16}$ gives $A = -13 \times 10^{12}$ J m^{-3}, and $\omega_y = 4.0 \times 10^{16}$ gives $A = -6 \times 10^{12}$ J m^{-3}, showing that A is not critically dependent on our choice of ω_y.

As a further check we may estimate the value of A by assuming

$$A_{xyz} \simeq \tfrac{1}{2}m(\omega_x^2 x^2 + \omega_y^2 y^2 + \omega_z^2 z^2)$$

when $x \simeq y \simeq z \simeq 1\text{Å}$. This gives $|A| \simeq 7 \times 10^{12}$ J m^{-3}.

We are now in a position to predict the SHG coefficient, using equations (4.24) and the numerical values $\omega_y = 3.0 \times 10^{16}$ rad.s^{-1} and $A = -8 \times 10^{12}$ J m^{-3}. We find

$$d_{14} = +11 \times 10^{-13} \text{ m V}^{-1}.$$

The experimental value is $\chi_{xyz} = 3.3 \times 10^{-9}$ e.s.u., i.e. $d_{14} = 7 \times 10^{-13}$ m V^{-1}, with the same sign as d_{11} in l-quartz[87]. Miller and Nordland[47] have found d_{11}(l-quartz) to be positive, giving

$$d_{14} = + 7 \times 10^{-13} \text{ m V}^{-1}.$$

Repeating the calculation for l-$NaBrO_3$, we once again select $\omega_y = 3.0 \times 10^{16}$ rad.s^{-1}, and find that $A = +5 \times 10^{12}$ J m^{-3}, and

$$d_{14} = -8 \times 10^{-13} \text{ m V}^{-1}.$$

Experimentally, $$d_{14} = -3 \times 10^{-13} \text{ m V}^{-1}.$$

The sign agreement is satisfying, while the numerical agreement is as good as can be expected from the crudeness of the calculation. Better agreement would be obtained by setting $\omega_y = 4.0 \times 10^{16}$ rad.s^{-1}, but such numerical manipulation seems physically unjustifiable, since it would lead to a very high force

constant for vibration along the y'-axis. A more likely explanation of the difference is to be found in the symmetry properties of the two effects. For the more general anharmonic potential

$$V = \tfrac{1}{2}m\omega_i^2 x_i'^2 + \tfrac{1}{6}A_{ijk}x_i'x_j'x_k' ,$$

only the terms with $i \neq j \neq k$ can contribute to optical activity, whereas all terms can contribute to SHG. The terms we have neglected will have the same order of magnitude, but not necessarily the same signs, as those we have retained. The same can be said of the geometric factors like C in equations (4.22) and (4.23). In these circumstances it is almost inevitable that some cancellation will occur.

Nevertheless, although no great reliance can be placed on the exact numerical values calculated in this chapter, the order of magnitude agreement demonstrates quite convincingly that Condon's one-electron anharmonic oscillator model can successfully account for both optical activity and SHG. This confirms our suspicion that similar distortions of the electronic wave-functions are responsible for the two effects. It should be noted that the one-electron model of optical activity provides a much more satisfactory account of SHG than the coupled

oscillator models (see, e.g., Kuhn[108]), which can show only a linear optical response, unless an anharmonic term is specially added[103].

Chapter 5

CONCLUSION

The important effects of geometry on nonlinear optical coefficients have already been stresseed by Robinson,[30] who calculated, on this basis, simple numerical relations between the NLO tensor elements of ZnS-type compounds. In chapter 2 we developed these ideas further to enable us to compare the nonlinear behaviour of different materials. The method of computing the geometric factor is new except, of course, for the use of the tensor transformation law. By assigning an empirically determined nonlinear polarisability to the acentric constituents of a crystal we allow in a simple and obvious way for packing density. This is important because it is only the acentric units of a material which contribute to nonlinear effects, whereas all atoms contribute to the linear susceptibility. The importance of using the Miller Δ to normalise out the effects of local fields in calculations of this sort has also been recognised by other workers (DiDomenico and Wemple[40], Levine[38]).

While this work can be claimed to apply to the electro-optic effect in addition to purely electronic

effects, its logical extension, the consideration of individual bonds, cannot. Thus ionic effects are excluded from chapter 3, which is therefore concerned with second-harmonic generation coefficients. The resulting NLO bond polarisability theory can be summarised as follows. Optical nonlinearities can be regarded as having their origin in the chemical bonds of a material: only the heteropolar covalent bonds are important. There is only one important NLO bond polarisability tensor element $\beta_{\parallel}$, making the tensorial addition of the effects of the various bonds quite straightforward. The effects of geometry are automatically included in this tensor sum. At this stage, the theory is frankly empirical. Nevertheless, it has enabled us to make useful sign predictions, and the connection between β and electronegativity and coordination should provide an estimate of the magnitude of the coefficients in new materials.

We may speculate that materials which may be discovered in the future will have NLO coefficients of about the same size as those already known. Barium titanate has a normal Miller $\triangle$ despite the anomalously large β of the Ti-O bond. It appears that the crystal structure compensates for the considerable acentricity

of the bonds by departing only slightly from the centrosymmetric perovskite structure. The Ti-O bond probably represents the upper limit of NLO bond polarisabilities; oxygen is the most electronegative element after fluorine while elements with electronegativities much below that of titanium are unlikely to form complex anions with oxygen. Better nonlinear optical materials are likely to result from improved crystal properties other than the intrinsic optical nonlinearities. To grow an optical quality crystal of sufficient size is not always easy. Other desiderata include general physical robustness, the ability to achieve phase-matching ~~along~~ perpendicular to the optic axis, and freedom from twinning and optically-induced damage at high light intensities.

The relationship between optical activity and nonlinear optical effects was investigated for its intrinsic interest, rather than for any merit it might have in assessing NLO coefficients. The geometric calculations are complex, and it is difficult to assign frequencies to the oscillator. However, without going into all these cumbersome details, it may be that optical rotatory power serves as a very rough guide to the size of optical nonlinearities. Certainly lithium iodate and iodic acid have larger coefficients

than quartz, sodium chlorate and sodium bromate for both phenomena.

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