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IN

FREQUENCY DOUBLING

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IN

### by

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## A Thesis

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DOCTOR OF PHILOSOPHY (1966) (Physics) McMASTER UNIVERSITY Hamilton Ontario.

TITLE: Frequency Doubling in NiSO<sub>4</sub>.6 H<sub>2</sub>O AUTHOR: Derwyn Carlyle Johnson, B.Sc. (McMaster University) SUPERVISOR: Professor R.G. Summers-Gill NUMBER OF PAGES: vii, 142 SCOPE AND CONTENTS:

Using a Q-spoiled Nd-glass laser, an experimental investigation of frequency doubling in NiSO<sub>4</sub>.6 H<sub>2</sub>O was carried out. The frequency doubling was observed to occur at a phase matching angle of  $56^{\circ} \pm 1^{\circ}$ . Experimentally, it is shown that the fundamental frequency at  $\lambda = 1.06 \ \mu\text{m}$  is an O-ray while the doubled frequency at  $\lambda = .53 \ \mu\text{m}$  is an E-ray. Since the amplitude for electric dipole frequency doubling in NiSO<sub>4</sub>.6 H<sub>2</sub>O is zero, these observations are unusual. The observations are attributed to magnetic dipole and/or electric quadrupole frequency doubling. Evidence to support this view comes from the magnitude of the effect and from its azimuthal dependence. The electric quadrupole type frequency doubling is consistent with the data only if the susceptibility coefficients satisfy the relation

 ${}^{\mathbb{Q}}\chi^{\text{EE}}_{1212} = \frac{1}{2} \left( {}^{\mathbb{Q}}\chi^{\text{EE}}_{1111} - {}^{\mathbb{Q}}\chi^{\text{EE}}_{1122} \right)$ 

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### CHAPTER I

#### INTRODUCTION

The physical phenomena that occur when light interacts with matter have always been of great interest to physicists. This interest has been stimulated further by the development of the laser as a high power coherent source of optical radiation. In particular, a new field of phenomena "nonlinear optics" has been created. The work reported in this thesis will be concerned with some of the experiments in this new field.

It is well known that when a light beam propagates through a medium, a polarization is induced. For conventional optical fields, the amplitude of the induced polarization varies linearly with the applied field. This is to be expected, since the fields in the atom are so large, that the externally applied field is only a small perturbation on the much larger local fields. The situation has changed with the availability of high power optical fields in laser light beams. With a laser light source, the observation of nonlinear effects is possible. The question may now be asked as to what sort of phenomena nonlinear effects might produce. Some of the qualitative features can be illustrated by making a scalar power series expansion of the induced polarization in terms of the electric field

$$P = a_1 E + a_2 E^2 + a_3 E^3 + \dots$$
 (1-1)

where  $a_1$  is the customary linear polarizability and  $a_2$  and  $a_3$  are the coefficients of the nonlinear terms. If it is assumed that a plane wave with electric field  $E=E_0 \cos \omega t$  is propagating through the medium, the induced polarization is given by

$$P = a_1 E_0 \cos \omega t + \frac{a}{2} E_0^2 (1 + \cos 2\omega t) + \frac{a}{4} E_0^3 (3\cos \omega t + \cos 3\omega t) + \dots (1-2)$$

The first term, an induced polarization at the frequency of the applied field, will radiate an electromagnetic wave at the fundamental frequency. It is this term which is responsible for a medium having a refractive index different from unity. The first nonlinear term produces a d.c. polarization and one at twice the frequency of the applied field. The zero frequency term will induce a voltage across the crystal, so this nonlinear effect is called optical rectification. On the other hand, the induced polarization at twice the frequency will radiate an electromagnetic wave at twice the frequency doubling or second harmonic generation (S.H.G.). In a similar manner, the next nonlinear term will produce frequency tripling or third harmonic generation (T.H.G.) and also will give rise to an intensity dependence of the refractive index.

Perhaps the most striking characteristic of nonlinear phenomena is the production of light at frequencies different from that of the applied field. The first successful observation of a nonlinear effect was performed by Franken <u>et al.</u> (1). In that experiment, the light from a ruby laser (.6943  $\mu$ m) was focused on a quartz platelet. The transmitted light was analysed with a spectrograph and a minute amount of doubled light at .3472  $\mu$ m was detected. The doubled frequency light was attributed to radiation from an electric dipole polarization at the doubled frequency which was induced by the laser light. This initial experiment was rapidly followed by others (2,3,4) in which enhanced frequency doubling and mixing were observed.

Besides frequency doubling other nonlinear effects have been observed. The optical rectification of light has been reported by Bass et al. (5). Third harmonic generation electric field induced frequency doubling and electric quadrupole frequency doubling were first observed by Terhune et al. (6). The latter two effects are of interest since they are small compared to electric dipole frequency doubling. Their observation was possible in calcite because the coefficients for electric dipole frequency doubling are zero in a crystal with a centre of symmetry. Since a surface has no centre of symmetry. it is possible to observe frequency doubling on reflection. This effect was first observed by Ducuing and Bloembergen (7). In that experiment, doubled frequency light was detected in the laser beam reflected from the surface of a gallium arsenide (GaAs) crystal. The last nonlinear effect that will be mentioned is the intensity dependent refractive index. The effect is due to an induced polarization proportional to three electric fields and has been observed by Maker et al. (8) in liquids.

The investigation reported in this thesis was motivated by the discovery of a different null condition on electric dipole frequency doubling. The amplitude for electric dipole frequency doubling can be zero for uniaxial negative crystals belonging to the point groups (422) and

(622). In the hope of observing some new nonlinear effects, an investigation of the frequency doubling in nickel sulphate hexahydrate  $(NiSO_4.6H_2O)$  was undertaken. This crystal is uniaxial negative and belongs to the point group 422.

### CHAPTER II

### THEORY

# (2-1) The Nonlinear Susceptibilities

In the preceding section, a scalar expansion of the induced polarization was used to illustrate nonlinear phenomena. For a crystal, such an expansion is not correct. It is well known, that there is a tensor relation between the induced polarization and the electric field. Furthermore, the effects of dispersion were neglected in the expansion. A more realistic series expansion of the ith component of the induced polarization is

$$P_{i} = P_{ij}^{E}(\omega) E_{j}(\omega) + P_{ijk}^{EE}(\omega = \omega - \omega) E_{j}(\omega) E_{k}(\omega)$$

$$+ P_{ijk}^{EE}(2\omega = \omega + \omega) E_{j}(\omega) E_{k}(\omega) + P_{ijkl}^{EVE}(2\omega = \omega + \omega) E_{j}(\omega) \nabla_{k}E_{l}(\omega)$$

$$+ P_{ijkl}^{EEE}(2\omega = \omega + \omega + \omega) E_{j}(\omega) E_{k}(\omega) E_{l}(\omega)$$

$$+ P_{ijk}^{EEE}(3\omega = \omega + \omega + \omega) E_{j}(\omega) E_{k}(\omega) E_{l}(\omega)$$

$$+ \dots \qquad (2-1)$$

where

$$X_{ij}^{E}(\omega)$$
 is the linear electric susceptibility,

 $\sum_{ij}^{P} X_{ij}^{EE}(o=\omega-\omega)$  is the coefficient for optical rectification,

 $\chi_{ijk}^{\text{EE}}(2\omega = \omega + \omega) \text{ is the coefficient for electric dipole}$ doubling.

 $\chi_{ijk}^{P EVE}$  (2 $\omega$ ) is the coefficient for electric quadrupole frequency doubling.

 $\gamma_{ijk}^{\text{EEE}}$  (2  $\omega$ ) is the coefficient for electric field induced frequency doubling.

and  $\gamma_{ijk}^{\text{EEE}}(3\omega)$  is the coefficient for frequency tripling.

The summation convention on repeated indices is implied. A complete expansion can also contain terms which are proportional to the magnetic field. In addition, there can be analogous series expansions of the induced magnetization and electric quadrupole polarization. It should be noted, that the coefficients for optical rectification and electric dipole frequency doubling are no longer related as they were in the scalar series expansion. In this way dispersive effects can be included in the expansion.

The number of independent coefficients in the susceptibility tensor is restricted by the crystal symmetry. This can be expressed in the principle that the susceptibility tensors must be invariant under all symmetry operations of the crystal point groups. Let  $A = A_{\alpha\beta}$  be a symmetry operator belonging to the point group of the crystal, where A is an orthogonal transformation, i.e. the inverse of A is equal to the transpose of A. Let the primed symbols represent the new quantities after transformation so that

 $P'_{\alpha} = A_{\alpha i} P_{i}$ 

Thus

becomes

and

$$E'_{\beta} = A_{\beta j} E_{j}$$

$$P_{i} = \chi_{ijk} \dots \ell E E \dots E_{jk} \ell$$

$$P'_{\alpha} = \chi'_{\alpha\beta\gamma} \dots \xi E_{\beta} E'_{\gamma} \dots E'_{\delta}$$

$$A_{\alpha i} P_{i} = \chi'_{\alpha\beta\gamma} \dots \xi A_{\beta j} A_{\gamma k} \dots A_{\delta \ell} E_{j} E_{k} \dots E_{\ell}$$

$$= A_{\alpha i} \chi_{ijk} \dots \ell E_{j} E_{k} \dots E_{\ell}$$

$$a_{\beta\gamma} \dots \xi = A_{\alpha i} \chi_{ijk} \dots \ell A_{j\beta} A_{k\gamma} \dots A_{\ell} \xi$$

Therefore  $\chi_{\alpha\beta\gamma}$ .

If the tensor is to be invariant under the symmetry operation A then

$$\chi_{\alpha\beta\gamma} \cdots s = {}^{A}_{\alpha i} {}^{A}_{\beta j} {}^{A}_{\gamma k} \cdots {}^{A}_{s \ell} \chi_{i j k} \dots \ell \qquad (2-2)$$

=  $A_{\alpha i} A_{\beta j} A_{\gamma k} \cdots A_{\delta \ell} \chi_{i j k} \dots \ell$ 

There will be as many equations (2-2) as there are symmetry operators belonging to the point group of the crystal. Equation (2-2) is valid only for polar tensors. Axial tensors can also occur in the expansion (2-1) when magnetic effects are included. For axial tensors the transformation equation becomes

$$\chi_{\alpha\beta\gamma} \cdots \varsigma = \pm A_{\alpha i} A_{\beta j} A_{\gamma k} \cdots A_{\delta \ell} \chi_{i j k} \cdots \ell \qquad (2-3)$$

The negative sign must be taken with symmetry operators which transform from a right handed coordinate system to a left handed system or vice versa. The plus sign is chosen for those symmetry operations in which the handedness of the coordinate system does not change.

As a relevant example, consider the case of electric dipole frequency doubling. In this case equation (2-2) becomes

 ${}^{P}\chi^{EE}_{\alpha\beta\gamma}(2\omega) = {}^{A}_{\alpha i} {}^{A}_{\beta j} {}^{A}_{\gamma k} {}^{P}\chi^{EE}_{i j k}(2\omega)$ 

For a crystal with a centre of symmetry, the inversion operator  $A = -\delta_{mn}$  belongs to the point group. Therefore,

$${}^{P}\chi^{EE}_{\alpha\beta\gamma}(2\omega) = (-\delta_{\alpha i}) (-\delta_{\beta j}) (-\delta_{\gamma k}) {}^{P}\chi^{EE}_{ijk}(2\omega) = - {}^{P}\chi^{EE}_{ijk}(2\omega) = o$$

This is the important null condition on the coefficients for electric dipole frequency doubling in crystals with a centre of symmetry. For crystals with no centre of symmetry, crystal symmetry will require some, but not all, of the components of a tensor to be zero.

The susceptibility tensors may also possess intrinsic symmetry depending on the nature of the physical process they describe. This additional symmetry will reduce the number of independent coefficients even further. In the case of electric dipole frequency doubling,  $P_i(2\omega) = {}^P\chi_{ijk}^{EE}(2\omega) E_j(\omega) E_k(\omega)$ , the fields  $E_j(\omega)$  and  $E_k(\omega)$  are indistinguishable. Hence the tensor  ${}^P\chi_{ijk}^{EE}(2\omega)$  is symmetric in its last two indices and

$${}^{\mathrm{P}}\chi^{\mathrm{EE}}_{\mathrm{ijk}}(2\omega) = {}^{\mathrm{P}}\chi^{\mathrm{EE}}_{\mathrm{ikj}}(2\omega).$$

On the other hand, in the case of sum or difference frequency generation.

$$P_{\mathbf{i}}(\omega_{\mathbf{j}}=\omega_{\mathbf{j}}\pm\omega_{\mathbf{j}}) = \frac{P_{\mathbf{j}}\chi_{\mathbf{i}\mathbf{j}\mathbf{k}}^{\text{EE}}(\omega_{\mathbf{j}}=\omega_{\mathbf{j}}\pm\omega_{\mathbf{j}}) \quad E_{\mathbf{j}}(\omega_{\mathbf{j}}) \quad E_{\mathbf{k}}(\omega_{\mathbf{j}}),$$

the fields are distinguishable. Hence the tensors  $\chi^{p}_{ijk} (\omega_3 = \omega_1 \pm \omega_2)$ are not required to be symmetric in the last two indices.

All crystals can be classified into 32 different point groups. The form of the susceptibility tensors can be determined for each using relations (2-2) and (2-3). Fortunately in the case of electric dipole frequency doubling, the symmetry restrictions on the coefficients are exactly the same as those for the piezoelectric coefficients. Hence the form of the electric dipole tensor  $\sum_{ijk}^{P} \sum_{ijk}^{EE} (2\omega)$  is the same as that of the piezoelectric tensor and can be found in most books on piezo-electricity (9). There is, however, no relation between the magnitude of the frequency doubling coefficients and the magnitude of the piezoelectric, i.e. no centre of symmetry and therefore suitable for frequency doubling.

Since the frequency doubling coefficients  $\chi_{ijk}^{\text{EE}}(2\omega)$  are symmetric in their last two indices, some authors have used the contracted tensor notation that is used in piezoelectricity. In this notation, a single index l, which can take on the values 1 to 6 replaces the last two indices j and k where.

$$l = 1$$
 2 3 4 5 6  
j,k = 1,1 2,2 3,3 2,3 1,3 1,2  
3,2 3,1 2,1

The most general frequency doubling tensor, corresponding to a triclinic crystal belonging to the point group 1, is given below in the contracted tensor notation  $\begin{bmatrix} & 2 \\ & E \end{bmatrix}$ 

•									x	
-	ר ה	ł	г					· 1	Е <sub>у</sub> 2	
	P X		<i>x</i> <sub>11</sub>	X <sub>12</sub>	<i>X</i> 13	$\chi_{14}$	X <sub>15</sub>	x <sub>16</sub>	Ez <sup>2</sup>	
	P y	9	$\chi_{_{21}}$	x <sub>22</sub>	X <sub>23</sub>	$\chi_{_{24}}$	$\chi_{_{25}}$	x <sub>26</sub>	2E <sub>y</sub> E <sub>z</sub>	
	Pz		x 31	X <sub>32</sub>	$\chi_{_{33}}$	X34	$\chi_{35}$	x_36	2E_E x z	
	ᆈ		L						2E_E x y	

There are 18 independent coefficients. This number will be reduced for point groups of higher symmetry. In the case of the other nonlinear susceptibility tensors the effect of crystal symmetry can be found, for both polar and axial tensors up to 4th order, in a review article by Birss (10). The effect of any intrinsic symmetry that the physics may require can be added.

Up to this point, nothing has been said about the magnitude of the nonlinear susceptibility coefficients. Rough order-of-magnitude values can be obtained theoretically. Using perturbation theory, Franken and Ward (11) have shown that the ratio of the electric dipole frequency doubling susceptibility to the linear susceptibility is of the order of the inverse atomic fields. They estimate the magnitude of the frequency doubling coefficient to be  $10^{-7}$  esu. In a measurement of the absolute magnitude of the nonlinear susceptibility, the experimenter encounters several difficulties which will be elaborated on in a later chapter. The most reliable value for the frequency doubling coefficient has been obtained by Ashkin <u>et al.</u> (12) using a gas laser. They measured a value of  $3 \times 10^{-9}$  esu for the  $\sum_{312}^{P}$  EE (2 $\omega$ ) coefficient in potassium dihydrogen phosphate (KDP). For the present the best experimental procedure is to measure the magnitude of the other nonlinear susceptibilities relative to that of KDP. If the electric fields are measured in statvolts per cm. the expected values of the susceptibilities in (2-1) are:

$${}^{P}\chi_{ij}^{E}(\omega) \sim 10^{-1}, {}^{P}\chi_{ijk}^{EE}(o) \sim 10^{-7}, {}^{P}\chi_{ijk}^{EE}(2\omega) \sim 10^{-9},$$
$${}^{P}\chi_{ijk}^{EEE}(2\omega = o^{+}\omega + \omega) \sim 10^{-13}, {}^{P}\chi_{ijk}^{EVE}(2\omega) \sim 10^{-16} \text{ and}$$

 $\chi_{ijk}^{\text{EEE}}$  (3 $\omega$ )~10<sup>-16</sup>. For comparison, the values of the susceptibilities in rationalized m.k.s. units are;

 ${}^{P}\chi_{ij}^{E}(\omega) \sim 10^{-11}, \qquad {}^{P}\chi_{ijk}^{EE}(\circ) \sim 10^{-22}, \qquad {}^{P}\chi_{ijk}^{EE}(2\omega) \sim 10^{-24}$  ${}^{P}\chi_{ijk}^{EEE}(2\omega) \sim 10^{-32}, \qquad {}^{P}\chi_{ijk}^{EVE}(2\omega) \sim 10^{-32} \text{ and}$  ${}^{P}\chi_{ijk}^{EEE}(3\omega) \sim 10^{-35}.$ 

#### (2-2) A Microscopic Theory of the Nonlinear Susceptibilities

In the first sub-section, a phenomenological description of the nonlinear susceptibilities was given. It is desirable to be able to calculate the nonlinear susceptibilities from first principles. The problem is similar to that of calculating the linear electric susceptibilities from a microscopic theory. This was first accomplished using the classical Lorentz-Drude model in which the medium was considered to be an assemblage of harmonic oscillators. An extension to include nonlinear effects may be made (13) by generalizing to the case of anharmonic oscillators. Although this simple model has its limitations, it yields almost as much insight into the nature of nonlinear phenomena as does a more rigorous quantum mechanical calculation.

The equation of motion of an anharmonically bound electron driven by an oscillating electric field E=E cosat is

$$\dot{x} + \omega_0^2 x + \alpha x^2 = -\frac{eE_0}{m} \cos \omega t. \qquad (2-4)$$

where x is the displacement of the electron,  $\omega_{0}$  is its resonant frequency in the harmonic limit,  $\alpha$  is a coefficient specifying the degree of nonlinearity, and e and m are the charge and mass of the electron respectively. If the nonlinearity is small it can be treated as a perturbation and solutions to (2-4) in the form of a Fourier series can be found by successive approximations. Assume a solution of the form

 $x = x_1 \cos \omega t + x_2 \cos 2\omega t$ 

Substituting this into (2-4) and equating coefficients of the same frequency, one can show that

 $x_1 = -\frac{eE_o}{m} \frac{1}{\omega^2 - \omega^2}$ 

and

$$x_{2} = -\frac{\alpha}{2} \frac{e^{2}E^{2}}{m^{2}} \frac{1}{(\omega_{0}^{2} - 4\omega^{2})(\omega_{0}^{2} - \omega^{2})^{2}}$$

If the medium has N oscillators per cubic centimeter, the induced polarizations are

$$P(\omega) = - \frac{Ne^2}{m(\omega_0^2 - \omega^2)} E_0 \equiv \chi^E(\omega) E_0 \qquad (2-5)$$

and

 $P(2\omega) = - \frac{N\alpha e^{3}}{2m^{2}} \frac{1}{(\omega^{2} - 4\omega^{2})(\omega^{2} - \omega^{2})^{2}} E_{0}^{2} = \chi_{(2\omega)}^{2} E_{0}^{2}$ An inspection of (2-5) shows the familiar increase in the linear sus-

ceptibility near an absorption band. There is an analogous increase in the second harmonic susceptibility when either the fundamental or the second harmonic is close to an absorption band. The infinite resonance can be made more realistic by introducing a damping term f in the equation of motion (2-4). The same model can also be used to calculate the other nonlinear susceptibilities in an analogous manner.

A more rigorous calculation of the nonlinear susceptibilities can be obtained from quantum mechanics. Extensive calculations using time dependent perturbation theory (11, 14, 15) and the equation of motion of the density matrix (16, 17, 18) have been carried out by many authors. For comparison with the susceptibilities in (2-5) the linear and electric dipole frequency doubling coefficients as determined from perturbation theory (15) will be quoted here. As before, with an applied field  $E(t) = E_0 \cos \omega t$  the susceptibilities are defined in terms of the field amplitude as

 $P_{i}(\omega) = \alpha_{ij}(\omega)E_{oj}(\omega)$ 

and

$$\alpha_{ij}(\omega) = \frac{e^2}{h} \sum_{n \in I} \langle r_i \rangle \langle r_j \rangle_{ng} \left[ \frac{1}{\omega_{ng} + \omega} + \frac{1}{\omega_{ng} - \omega} \right]$$

 $P_{i}(2\omega) = \beta_{ijk}(2\omega) E_{oj}(\omega) E_{ok}(\omega)$ 

and

where

$$\beta_{ijk}(2\omega) = -\frac{e^3}{4h^2} \left\{ \sum_{nm} \langle \mathbf{r}_i \rangle_{gn} \left[ \langle \mathbf{r}_j \rangle_{mn} \langle \mathbf{r}_k \rangle_{mg} + \langle \mathbf{r}_j \rangle_{mg} \langle \mathbf{r}_k \rangle_{mn} \right] \right.$$
$$\cdot A_{nm} + \langle \mathbf{r}_i \rangle_{mn} \langle \mathbf{r}_j \rangle_{mg} \langle \mathbf{r}_k \rangle_{ng} B_{mn} \right\}$$

where

$$A_{nm} = \frac{1}{(\omega_{ng} - 2\omega)(\omega_{mg} - \omega)} + \frac{1}{(\omega_{ng} + 2\omega)(\omega_{mg} + \omega)}$$
$$B_{mn} = \frac{1}{(\omega_{mg} - \omega)(\omega_{ng} + \omega)} + \frac{1}{(\omega_{mg} + \omega)(\omega_{ng} - \omega)}$$

These susceptibilities only apply to an isolated atomic system. The summations are extended over the electronic excited states n,m of the atom where  $f_1 \omega_{ng}$  is the energy of the nth state above the ground state and  $\langle r_i \rangle$  is the matrix element of the ith component of the position gn operator r between the ground state g and the excited state n. The frequency doubling susceptibility contains the product of three matrix elements. Each product vanishes identically for an atomic system that is invariant under inversion symmetry. Hence the symmetry requirements on this coefficient come naturally out of the theory.

The linear susceptibility has been extended to dense media by Lorentz (19) to give the familiar expression for cubic crystals.

$$\chi_{ij}(\omega) = N \frac{\mathcal{E}(\omega) + 2}{3} \alpha_{ij}(\omega)$$

where N is the number of atoms per unit volume. Using a similar sort of analysis Armstrong <u>et al</u>. (14) have also extended the frequency doubling coefficient to dense media

$$\chi_{ijk}(2\omega) = N \left[\frac{\varepsilon(\omega)*2}{3}\right]^2 \left[\frac{\varepsilon(2\omega)*2}{3}\right]^{\beta}_{ijk}(2\omega)$$

where  $\mathcal{E}(\omega)$  and  $\mathcal{E}(2\omega)$  are the dielectric constants at the fundamental and second harmonic frequencies respectively.

### (2-3) Wave Propagation in Nonlinear Media

In this section, it will be assumed that a macroscopic nonlinear polarization exists and its effect on a wave propagating in a nonlinear medium will be determined. In particular, it will be assumed that a plane wave  $\overline{E}(\omega) = \overline{E}_0 e^{i(\overline{E}_1 \cdot \overline{r} - \omega t)}$  at the frequency  $\omega$  propagating through a nonlinear medium will induce a polarization  $\overline{F}(2\omega) = \hat{\chi} : \overline{E}_0 \overline{E}_0 e^{i(2\overline{E}_1 \cdot \overline{r} - 2\omega t)}$  at the doubled frequency. The problem will be to determine the intensity of the doubled frequency light that is produced. Firstly, it should be noted that the polarization at the doubled frequency propagates through the medium with the same phase velocity as the wave at the fundamental frequency. Since most materials have dispersion at optical frequencies, the electromagnetic wave radiated by the nonlinear polarization will propagate through the medium at a different phase velocity. The doubled frequency light will soon be out of phase with the polarization that is generating it. There will be destructive interference and the intensity

will be limited. If the indices of refraction of the fundamental and the doubled frequencies should happen to be the same, the doubled frequency intensity could be large. The importance of conserving electromagnetic momentum in the frequency doubling process will be illustrated in the following calculations.

A practical problem as far as experimental nonlinear optics is concerned, is to determine the amount of doubled frequency radiation produced in a platelet of thickness  $\ell$ . The simplified calculation given here follows that given by Naiman et al. (20). It will be assumed that the light is incident normally at z=o on the surface of an infinite slab of nonlinear material. The geometry for the calculations and the relevant quantities are shown in Figure 1. The effect of absorption at both the fundamental and the doubled frequency has been included in a linear fashion by allowing the refractive indices to be complex. All the quantities listed in Figure 1 are values in the medium. The effect of boundaries has been treated in detail by Bloembergen and Pershan (21) and will be neglected here. The depletion of the fundamental frequency wave through its conversion into doubled frequency will also be neglected. This is a good approximation experimentally, since the conversion efficiencies are usually low.

The starting point for the calculation is Maxwell's equations in which the induced polarization  $\overline{P}(\omega) = \hat{\chi} : \overline{E} \overset{\circ}{E} \overset{\circ}{e} e^{i(2\overline{k}_1 \cdot \overline{r} - 2\omega t)}$ is treated as a source term for doubled frequency light

## Figure 1

### Frequency Doubling in an Infinite Nonlinear Platelet

All the waves are propagating in the direction of the z-axis. The quantities  $n(\omega)$  and  $n(2\omega)$  are the complex refractive indices,  $k_1$  and  $k_2$  the wave numbers, and  $\alpha_1$  and  $\alpha_2$  the amplitude absorption coefficients at the frequencies  $\omega$  and  $2\omega$  respectively.



$$\nabla \cdot \vec{E}(2\omega) = o$$

$$\nabla \cdot \vec{E}(2\omega) = o$$

$$\nabla \times \vec{E}(2\omega) = -\frac{1}{c} \frac{\partial}{\partial t} \vec{E}(2\omega)$$

$$\nabla \times \vec{E}(2\omega) = -\frac{1}{c} \frac{\partial}{\partial t} \vec{E}(2\omega) \vec{E}(2\omega) + \frac{4\pi}{c} \frac{\partial}{\partial t} \vec{F}(2\omega) .$$
(2-6)

These equations can be combined to form an inhomogeneous wave equation for the electric field at the doubled frequency

$$\nabla^2 \, \overline{E}(2\omega) + \frac{4\omega^2}{c^2} \, \mathcal{E}(2\omega) \, \overline{E}(2\omega) = -\frac{16\pi\omega^2}{c^2} \, \hat{\chi} : \overline{E}_0 \, \overline{E}_0 e^{2i\overline{k}_1 \cdot \overline{r}} \, .$$

For the geometry chosen all the waves are propagating in the z direction, and the equation reduces to

$$\frac{d^2}{dz^2} \vec{E}(2\omega) + k_2^2 \vec{E}(2\omega) = -\frac{16\pi\omega^2}{c^2} \hat{\chi} : \vec{E}_0 \vec{E}_0 e^{2ik_1 z}$$

where  $k_2 = \frac{2\omega}{c} (n_2 + i s_2)$  and  $k_1 = \frac{\omega}{c} (n_1 + i s_1)$ . Taking the scalar product of the equation with  $\overline{e}_2$ , a unit vector in the direction of  $\overline{E}(2\omega)$ , one obtains

$$\frac{d^2}{dz^2} E(2\omega) + k_2^2 E(2\omega) = -\frac{16\pi\omega^2}{c^2} \chi_E^2 e^{2ik_1 z}$$
(2-7)

where  $\chi = (\bar{e}_2 \cdot \hat{\chi} : \bar{e}_1 \bar{e}_1)$  and  $\bar{e}_1$  is a unit vector in the direction in which  $\bar{E}(\omega)$  is polarized. The solution of (2-7) which satisfies the boundary condition  $E(2\omega)=0$  at z=0 is

$$E(2\omega) = -\frac{16 \pi \omega^2 \chi_{E_0}^2}{c^2 (k_2^2 - 4k_1^2)} \left[ e^{2ik_1 z} - e^{ik_2 z} \right]$$

or  

$$E(2\omega) = -i \frac{8\pi \chi E_o^2}{\eta_2^2 - \eta_1^2} e^{i\left(\frac{2k_1 + k_2}{2}\right)z} \sin\left(\frac{2k_1 - k_2}{2}\right)z$$

where  $\eta_1 = n_1 + i s_1$  and  $\eta_2 = n_2 + i s_2$ .

The intensity of the doubled frequency at  $z = \ell$  can be found from the magnitude of Poynting's vector

$$S(2\omega) = \frac{c n_2}{8\pi} |E(2\omega)|^2$$
  
=  $\frac{c n_2}{8\pi} |64\pi^2| \chi E_0^2|^2 \frac{|\sin \frac{\omega}{c}(\eta_1 - \eta_2)\ell|^2}{|\eta_2^2 - \eta_1^2|^2} e^{-2\frac{\omega}{c}(s_1 + s_2)\ell}$ 

Since

$$\left| \eta_{2}^{2} - \eta_{1}^{2} \right| = \left[ (n_{1} + n_{2})^{2} + (s_{1} + s_{2})^{2} \right] \left[ (n_{1} - n_{2})^{2} + (s_{1} - s_{2})^{2} \right]$$

and

$$\left|\sin\frac{\omega}{c}(\eta_1-\eta_2)\right|^2 = \sin^2\frac{\omega}{c}(\eta_1-\eta_2)\ell + \sinh^2\frac{\omega}{c}(s_1-s_2)\ell$$

the intensity reduces to

$$S(2\omega) = 8\eta c n_2 \left| \chi_{E_0}^2 \right|^2 \frac{\sin^2 \frac{\omega}{c} (n_1 - n_2) \ell + \sinh^2 \frac{\omega}{c} (s_1 - s_2) \ell}{\left[ (n_1 + n_2)^2 + (s_1 + s_2)^2 \right] \left[ (n_1 - n_2)^2 + (s_1 - s_2)^2 \right]} e^{-2\frac{\omega}{c} (s_1 + s_2) \ell}$$
(2-8).

In the limit of negligible absorption  $(s_1, s_2 \sim o)$ , the amount of doubled frequency produced in a transparent platelet becomes

$$S(2\omega) = 8\pi c n_2 \left| \chi_{E_0^2} \right|^2 \left[ \frac{\sin^2 \frac{\omega}{c} (n_1 - n_2) \ell}{(n_1^2 - n_2^2)^2} \right]$$
(2-9).

The doubled frequency intensity is seen to have an oscillatory behaviour as a function of crystal thickness. This arises because the doubled frequency radiation gets out of phase with the polarization that is generating it if  $n_1 \neq n_2$ . The effect has been observed by Maker <u>et al.</u> (3). From equation (2-9) it is possible to define a coherence length which is a measure of the distance that the doubled frequency radiation must propagate before it will be out of phase by  $\mathcal{T}$  with the polarization that is generating it. In one coherence length, the amount of second harmonic output will vary from zero to its maximum value. Hence  $\frac{\omega}{c}(n_1-n_2) \ l_{coh} = \frac{\mathcal{T}}{2}$  or  $\ l_{coh} = \frac{\lambda}{4(n_1-n_2)} = \frac{\lambda}{4\Delta n}$ . For crystals with typical dispersion in the visible  $\ l_{coh}$  varies from 5 $\lambda$  to 20 $\lambda$ .

Of particular interest is the case when  $n_1 = n_2 = n$ , which corresponds to the conservation of electromagnetic momentum in the frequency doubling process, i.e.  $k_2 = 2k_1$ . This is a special case of the more general momentum condition  $\bar{k}(\omega) + \bar{k}(\omega) = \bar{k}(2\omega)$  for waves that are not colinear. In the special case, the fundamental and doubled frequencies propagate through the crystal with the same phase velocity and equation (2-9) reduces to

$$S(2\omega) = 2\pi |\chi_{E_0}^2|^2 \frac{\omega^2 \ell^2}{nc}$$
 (2-10)

The oscillatory behaviour has disappeared and the intensity of the doubled frequency is seen to grow as the square of the crystal thickness. Expression (2-10) can only represent the initial growth in the doubled frequency power, since it is not valid to neglect the decrease in the strength of the fundamental when a large amount of doubled frequency is produced.

The formula for the amount of doubled frequency produced in an absorbing crystal at phase matching is of interest for the work reported in this thesis. For  $n_1=n_2=n$  equation (2-8) reduces to

$$S(2\omega) = 8\pi cn \left| \chi_{E_0}^2 \right|^2 \frac{\sinh^2 \frac{\omega}{c} (s_1 - s_2) \ell}{\left[ 4n^2 + (s_1 + s_2)^2 \right] \left[ s_1 - s_2 \right]^2} e^{-2 \frac{\omega}{c} (s_1 + s_2) \ell}$$

In terms of the amplitude absorption coefficients,  $\alpha_1 = \frac{\omega}{c} s_1$  and  $\alpha_2 = 2\frac{\omega}{c} s_2$ , the expression becomes

$$S(2\omega) = A e^{-\gamma l} \frac{\sinh^2 \xi l}{\xi^2}$$
(2-11a)  
where  $\xi = \begin{vmatrix} \alpha_1 - \frac{1}{2}\alpha_2 \end{vmatrix}$ ,  $\gamma = 2\alpha_1 + \alpha_2$ ,

and

$$A = \frac{2 \pi |\chi_{E_0}^2|^2}{\left[1 + \frac{\lambda^2 \gamma^2}{64 \eta^2 n^2}\right]} \frac{\omega^2}{nc} . \qquad (2-11b)$$

It can be seen that there is an optimum thickness for which the maximum amount of doubled frequency will be emitted from the platelet. This optimum thickness occurs when

$$\left[\frac{d \ S(2\omega)}{d \ l}\right]_{l=l_{m}} = 0$$

yielding the condition

$$\tanh \xi l_m = \frac{2\xi}{\gamma} . \qquad (2-12)$$

The above expressions have shown the significant increase in doubled frequency intensity that can be obtained when the indices of refraction at the fundamental and second harmonic frequencies are the Since all materials have dispersion at optical frequencies same. phase velocity matching is usually not possible. Nevertheless, there is a method of phase matching in some anisotropic materials, which makes use of optical birefringence to overcome the dispersion that is present in the material. The case of a uniaxial negative crystal will be discussed. However, this phase matching technique can also be applied to uniaxial positive and biaxial crystals. In uniaxial negative crystals light can propagate in two modes one as O-ray and the other as an E-ray and each mode has a different phase velocity or refractive index. The O-ray index is isotropic, but the E-ray index is not. In Figure 2 the solid lines represent the index surfaces at the fundamental frequency while the dashed lines are the index surfaces at the doubled frequency. The latter are outside the corresponding ones for the lower frequency since the crystal has been assumed to have normal dispersion. The Oray surfaces are spheres. A wave will propagate in O-ray mode if it is polarized perpendicular to a principal plane i.e. a plane containing the optic axis and the direction of propagation. On the other hand, the E-ray surfaces are ellipsoids of revolution and a wave will propagate in this mode if it is polarized in a principal plane. If the dispersion is not too large the O-ray sphere for the fundamental frequency will intersect the E-ray ellipsoid of revolution for the doubled frequency. This is shown in Figure 2. Hence an O-ray wave at the fundamental frequency propagating in the direction of the intersection will have the

### Figure 2

### Velocity Matching in a Negative Uniaxial Crystal

The solid lines are the index surfaces at the fundamental frequency while the dashed lines are the index surfaces at the doubled frequency. The O-ray surfaces are spheres and therefore isotropic whereas the E-ray surfaces are ellipsoids of revolution. The refractive index,  $n^{e}(\theta)$ , of the E-ray is a function of the angle  $\theta$  between the optic axis and the direction of propagation. For clarity, both the birefringence and the dispersion have been exaggerated in the diagram.



same refractive index as an E-ray at the doubled frequency propagating in the same direction. The two waves are said to be phase matched. It should be noted that the phase matching directions form a cone of half angle  $\theta_m$  about the optic axis which is given by

$$\sin \theta_{\rm m} = \sqrt{\frac{\frac{1}{(n_1^{\circ})^2} - \frac{1}{(n_2^{\circ})^2}}{\frac{1}{(n_2^{\circ})^2} - \frac{1}{(n_2^{\circ})^2}}} \qquad (2-13)$$

Phase matching so that two O-rays at the fundamental frequency produce an E-ray at the doubled frequency is not the only type of phase matching that is possible in a uniaxial negative crystal. An O-ray and an E-ray at the fundamental frequency can also combine to produce a phasematched E-ray at the doubled frequency. For colinear waves, the conservation of momentum condition requires that  $k_1^{0} + k_1^{e} = k_2^{e}$  or

$$n_2^{e}(\theta_m) = \frac{1}{2} \left[ n_1^{o} + n_1^{e}(\theta_m) \right]$$
 (2-14)

where

$$n_{1}^{e}(\theta) = \left[\frac{1}{n_{1}^{o^{2}}} + \left(\frac{1}{n_{1}^{e^{2}}} - \frac{1}{n_{1}^{o^{2}}}\right) \sin^{2}\theta\right]^{-\frac{1}{2}}$$

and

$$n_{2}^{e}(\theta) = \left[\frac{1}{n_{2}^{o^{2}}} + \left(\frac{1}{n_{2}^{e^{2}}} - \frac{1}{n_{2}^{o^{2}}}\right) \sin^{2}\theta\right]^{-\frac{1}{2}}$$

Equation (2-14) is not easily solved for  $\theta_{m}$ , since it is of the 4th degree in  $\sin^2 \theta_{m}$ . When necessary in this thesis, the two types of phase matching will be distinguished by denoting the first as OO-E and the

second as OE-E. The former is possible in uniaxial negative crystals for which  $n_2^{e} \leq n_1^{o}$  while OE-E type phase matching has the more restrictive requirement  $n_2^{e} \leq \frac{1}{2} (n_1^{e} + n_1^{o})$ .

The expressions (2-10) and (2-11) cannot be applied directly to interpret experiments in doubled frequency production in uniaxial crystals at phase matching. In the experimental situation, it is necessary to use a diverging pencil of rays for frequency doubling rather than the plane wave of infinite cross section assumed in the derivation. At phase matching not all the rays in the pencil can be truly along the phase matching direction. The problem is to determine how much second harmonic is produced by a ray close to phase matching. For the case of 00-E phase matching, as the propagation direction approaches  $\theta = \theta_m$ , the difference  $n_1^{0} - n_2^{e}(\theta)$  becomes very small resulting in the coherence length becoming very large. Expanding  $n_2^{e}(\theta)$  about  $\theta_m$  the difference is

$$n_1^{\circ} - n_2^{\circ}(\theta) = \left[\frac{\partial n_2^{\circ}(\theta)}{\partial \theta}\right] \delta$$
  
 $\theta = \theta_m$ 

where  $\delta = \theta - \theta_{\rm m}$  is the deviation of the ray from phase matching. After substituting this expression in (2-9), the second harmonic intensity for a ray close to phase matching becomes

s(2
$$\omega$$
) = 2 $\eta$   $|\chi_{E_0^2}|^2 \frac{\omega^2 \ell^2}{n_1^\circ c} \frac{\sin^2 \mu}{\mu^2}$   
where  $\mu \equiv \frac{\omega}{c} \left| \frac{\partial n_2^{e}(\theta)}{\partial \theta} \right|_{\theta = \theta_{m}} S\ell = \beta \ell \delta$  and

$$\beta = \frac{\pi}{\lambda} n_1 o^3 \left( \frac{1}{n_2^e} - \frac{1}{n_2^o} \right) \sin 2\theta_m \, d_m$$

This expression is the same as (2-20) except for the presence of a factor  $\frac{\sin^2 \frac{\gamma}{\gamma}}{\frac{\gamma^2}{\gamma^2}}$  which is a measure of the efficiency with which a ray close to phase matching will generate doubled frequency.

For the case of a bundle of rays with a finite divergence, the function  $\frac{\sin^2 \mu}{\mu^2}$  must be averaged over all directions in the bundle. The averaging has been done by Kleinman (22), who has shown that for a pencil of uniformly distributed rays with the central ray along a phase matching direction and the extremum rays diverging at an angle  $\Delta$  from it, the average is

$$\left\langle \frac{\sin^2 \psi}{\psi^2} \right\rangle = F(\beta \ell \Delta) = \frac{4}{\eta^2 \Delta} \int_0^{\Delta} (1 - \frac{\xi^2}{\Delta^2})^{\frac{1}{2}} \frac{\sin^2 \beta \ell \xi}{\beta^2 \ell^2 \xi^2} d\xi$$

Hence the intensity of second harmonic produced by the pencil is

$$S(2\omega) = 2\pi \left| \chi_{E_0}^2 \right|^2 \frac{\omega^2 \ell^2}{n c} F(\beta \ell \Delta)$$

The function  $F(\beta l \Delta)$  is a measure of the relative efficiency with which doubled frequency is generated by a pencil of rays with divergence 2 $\Delta$ compared to what would have prevailed if there had been no divergence. Depending on the value of  $\beta l \Delta$ , two limiting cases can be distinguished. For a thin crystal or a very nearly parallel beam,  $\beta l \Delta \ll 2$ , the function has the value

$$F(\beta l \Delta) = 1 - \frac{(\beta l \Delta)^2}{12} + \dots$$
In this case most of the rays in the pencil generate doubled frequency with maximum efficiency. For a thick crystal or widely diverging beam,  $\beta l \Delta >> 2$ .

$$F(\beta \ell \Delta) = \frac{2}{\beta \ell \Delta} - \frac{4}{\gamma (\beta \ell \Delta)^2} + \dots$$

Here most of the rays in the pencil are not very effective in producing doubled frequency. In fact, the second harmonic intensity increases only as  $\ell$  instead of  $\ell^2$ .

The above considerations have also been extended to absorbing crystals (23). Substituting the expansion for  $n_1^{o} - n_2^{e}(\theta)$  into equation (2-8), the second harmonic intensity for a ray close to phase matching is

$$S(2\omega) = A e^{-\gamma l} \frac{\sin^2 \beta l \delta + \sinh^2 \xi l}{\beta^2 \delta^2 + \xi^2}$$

where the constants A,  $\gamma$  and  $\dot{\xi}$  were defined previously in (2-11b). The average value of  $\frac{\sin^2 \beta \ell \hat{\xi} + \sinh^2 \hat{\xi} \ell}{\beta^2 \hat{\xi}^2 + \hat{\xi}^2}$  for a pencil of diverging rays is

$$F(\Delta,\xi) = \frac{4}{7\Delta} \int_{0}^{\Delta} (1-\frac{\xi^{2}}{\Delta^{2}}) \frac{\sin^{2}\beta l \xi + \sinh^{2}\xi l}{\beta^{2} \xi^{2} + \xi^{2}} d\xi.$$

As before, there are two limiting cases, a nearly parallel beam and a widely diverging beam. However, the average also depends on absorption. If  $\alpha_1 \approx 2\alpha_2$ , then  $\xi \approx 0$  and

$$F(\Delta, \frac{1}{5}) = \ell^{2} \left[ 1 + \frac{5^{2} \ell^{2}}{4} - \frac{(\beta \ell \Delta)^{2}}{12} + \dots \right]$$

for a nearly parallel beam. Neglecting all but the first term, the second harmonic intensity is  $S(2\omega) = A \ell^2 e^{-\gamma \ell}$ . On the other hand, for a widely diverging beam, it can be seen that the intensity is proportional to  $\ell e^{-\gamma \ell}$ . If  $\xi >> 0$ , then for a nearly parallel beam,

$$F(\Delta, \xi) = \frac{\sinh^2 \xi \mathcal{L}}{\xi^2} \left[ 1 - \frac{(\beta \ell_{\Delta})^2}{4} \left( \frac{1}{\xi^2 \ell^2} - \frac{1}{\sinh^2 \xi \mathcal{L}} \right) + \dots \right]$$

and to first order the second harmonic intensity is the same as that given for a ray in equation (2-11). While for a widely diverging beam, the intensity becomes

$$S(2\omega) = A \frac{e^{-\gamma l} \sinh \xi l}{\beta \xi \Delta}$$
.

In the preceding calculations, the intensities have been those inside the platelet, while the ones that are measured are outside the crystal. A correction for losses due to Fresnel reflections at the surfaces is necessary. For a crystal platelet in air and phase matching direction normal to the surface, the appropriate correction factor is  $R = \frac{64n^3}{(n+1)^6} (22).$  The final expressions, as they will be used later, for the amount of doubled frequency that is emitted from a transparent and an absorbing platelet of thickness  $\mathcal{L}$  are written in (2-15c) and (2-15b) respectively:

$$s(2\omega) = R 128 \pi^3 |\chi|^2 s^2(\omega) \frac{\omega^2 \ell^2}{c^{3_n^3}} F(\Delta \ell \beta)$$
 (2-15a)

$$S(2\omega) = R 128 \eta^3 |\chi|^2 s^2(\omega) \frac{\omega^2 \ell^2}{c^3 n^3} K$$
 (2-15b)

where  $S(\omega)$  and  $S(2\omega)$  are now the intensities of the fundamental and second harmonic frequencies outside the platelet. In (2-15b) the effects of absorption and beam divergence have been lumped together in the quantity K given by

$$K = \frac{e^{-\gamma \ell} \cdot F(\dot{\xi}, \Delta)}{\left[1 + \frac{\lambda^2 \gamma^2}{64\eta^2 n^2}\right] \ell^2} \approx \frac{e^{-\gamma \ell} \cdot F(\dot{\xi}, \Delta)}{\ell^2} \qquad (2-15c)$$

for  $\frac{\lambda^2 \gamma^2}{64 \eta^2 n^2} << 1.$ 

The process of phase matching in a uniaxial crystal is easily measured by monitoring the amount of doubled frequency produced as the angle  $\theta$  between the optic axis and the beam direction is passed through the phase matching angle. The observed variation in second harmonic as a function of the angle  $\theta$  is denoted as the phase matching curve. Since for a ray close to phase matching the second harmonic intensity varies as  $\frac{\sin^2 \frac{\gamma}{\mu}}{\mu^2}$  where  $\frac{\gamma}{\mu} = \beta l \delta = \frac{T}{2} \frac{l}{l_{coh}}$ , the phase matching curve for a parallel beam has a finite width due to the increase in coherence length close to phase matching. Once the coherence length of the ray is greater than the thickness of the crystal it will produce doubled frequency with almost maximum effectiveness. Hence only an infinitely thick crystal will have an infinitely narrow phase matching curve. For a crystal of thickness  $\mathcal L$  , the full width at half maximum of the phase matching curve is  $W = \frac{2.784}{\beta L}$ . If the beam has a divergence 2 $\Delta$ , there are two limiting cases; one where  $2\Delta << W$  and the width of the curve will be nearly the same as that for a parallel beam, and the other where  $2\Delta >> W$  and the width of the curve will be essentially equal to  $2\Delta$ . For an absorbing crystal

and a parallel beam, the width of the phase matching curve can be found by solving the transcendental equation

$$\sin^2 \frac{\beta l W}{2} = \frac{1}{2} \left( \frac{\beta^2 W^2}{4 \xi^2} - 1 \right) \sinh^2 \xi l$$

Unlike a transparent crystal, the width approaches a constant value  $2\frac{\xi}{\beta}$  (for  $\xi > 0$ ) with increasing thickness. In other respects, the width of the phase matching curve is similar to that for a transparent crystal.

# (2-4) The Time Averaged Free Energy

The object of this section is to demonstrate the existence of a time averaged thermodynamic function, the free energy, from which the various nonlinearities can be derived. This function can also be used to describe the usual electro- and magneto-optic effects. In addition, new symmetry relations among the various linear and nonlinear susceptibilities can be illustrated.

It will prove useful in this section to adopt the convention of writing the fields as

$$\overline{\tilde{\mathcal{E}}}(t) = \overline{E}(\omega) e^{i\omega t} + \overline{E}(\omega) e^{-i\omega t}$$
$$= 2\operatorname{Re}\left[\overline{E}(\omega) e^{i\omega t}\right].$$

Again one starts with Maxwell's equations for macroscopic media

$$\overline{\nabla} \cdot \overline{\mathcal{E}} = 47 \rho, \quad \overline{\nabla} \cdot \overline{\mathcal{B}} = o$$

$$\overline{\nabla} \times \overline{\mathcal{E}} = -\frac{1}{c} \quad \frac{\partial \overline{\mathcal{B}}}{\partial t} , \qquad \overline{\nabla} \times \overline{\mathcal{B}} = \frac{477}{c} \overline{\mathcal{J}} + \frac{1}{c} \frac{\partial \overline{\mathcal{E}}}{\partial t}$$

$$\rho = -\overline{\nabla} \cdot \overline{\mathcal{B}} + \overline{\nabla} \overline{\mathcal{P}} : \overline{\mathcal{A}}$$

$$\overline{\mathcal{J}} = \frac{\partial}{\partial t} \overline{\mathcal{P}} + c \ \overline{\nabla} \times \overline{\mathcal{M}} - \frac{\partial}{\partial t} \ \overline{\nabla} \cdot \overline{\mathcal{A}}$$

 $\overline{\mathcal{P}}$  is the electric dipole moment per unit volume,  $\overline{\mathcal{M}}$  is the magnetic dipole moment per unit volume, and  $\overline{\mathcal{Q}}$  is the electric quadrupole moment per unit volume. These equations can be combined in the customary way (24) to form the conservation of energy equation

where

$$\frac{c}{4\eta \tau} \overline{\nabla} \cdot (\overline{\tilde{\mathcal{E}}} \times \overline{\mathcal{H}} - \frac{4\eta \tau}{c} \overline{\tilde{\mathcal{E}}} \frac{\partial \overline{\tilde{\mathcal{A}}}}{\partial t}) + \frac{1}{4\eta \tau} \overline{\mathcal{H}} \cdot \frac{\partial \overline{\mathcal{B}}}{\partial t} + \frac{1}{4\eta \tau} \overline{\tilde{\mathcal{E}}} \cdot \frac{\partial \overline{\tilde{\mathcal{D}}}}{\partial t} + \overline{\nabla} \overline{\tilde{\mathcal{E}}}; \frac{\partial \overline{\tilde{\mathcal{A}}}}{\partial t} = c$$
or  $\overline{\nabla} \cdot \overline{\mathcal{S}} + \frac{1}{4\eta \tau} \overline{\mathcal{H}} \cdot \frac{\partial \overline{\mathcal{H}}}{\partial t} + \frac{1}{4\eta \tau} \overline{\tilde{\mathcal{E}}} \cdot \frac{\partial \overline{\tilde{\mathcal{E}}}}{\partial t} + \frac{\partial 2\ell}{\partial t} = c$ 
where  $\frac{\partial 2\ell}{\partial t} = \overline{\tilde{\mathcal{E}}} \cdot \frac{\partial \overline{\tilde{\mathcal{B}}}}{\partial t} + \overline{\mathcal{H}} \cdot \frac{\partial \overline{\tilde{\mathcal{M}}}}{\partial t} + \overline{\nabla} \overline{\tilde{\mathcal{E}}}; \frac{\partial \overline{\tilde{\mathcal{A}}}}{\partial t}$  (2-16)
and  $\overline{\tilde{\mathcal{B}}} = \overline{\mathcal{H}} + 4\eta \overline{\tilde{\mathcal{M}}}$  and  $\overline{\tilde{\mathcal{D}}} = \overline{\tilde{\mathcal{E}}} + 4\eta \overline{\tilde{\mathcal{P}}}.$ 

The first term  $\overline{\nabla} \cdot \overline{S}$  represents the rate at which energy is flowing out of a unit volume element. The next two terms,  $\frac{1}{477} \overrightarrow{\mathcal{H}} \cdot \frac{\partial \overrightarrow{\mathcal{H}}}{\partial t} + \frac{1}{477} \overrightarrow{\mathcal{E}} \cdot \frac{\partial \overrightarrow{\mathcal{E}}}{\partial t}$ , represent the rate at which the energy density in the electromagnetic field is changing and the last,  $\frac{\partial \cancel{\mathcal{H}}}{\partial t}$ , is the rate at which work per unit volume is being done on the medium by the external fields.

For the present, the discussion will be limited to the electric dipole term for which the material energy density is  $\frac{\partial \mathcal{U}}{\partial t} = \overline{\mathcal{E}}(t) \cdot \frac{\partial \overline{\mathcal{P}}(t)}{\partial t}$ . Assume the fields can be Fourier analyzed into n interacting waves. Then

$$\tilde{\mathcal{E}}(t) = 2\operatorname{Re} \sum_{\nu=1}^{n} \tilde{E}(\omega_{\nu,t}) e^{i\omega_{\nu}t} = \sum_{\nu=1}^{n} \left[ \tilde{E}(\omega_{\nu,t}) e^{i\omega_{\nu}t} + \tilde{E}^{*}(\omega_{\nu,t}) e^{-i\omega_{\nu}t} \right]$$

$$\vec{p}(t) = 2\operatorname{Re} \sum_{\nu=1}^{n} \vec{P}(\omega_{\nu}, t) e^{i\omega_{\nu}t} = \sum_{\nu=1}^{n} \left[ \vec{P}(\omega_{\nu}, t) e^{i\omega_{\nu}t} + \vec{P}*(\omega_{\nu}, t) e^{-i\omega_{\nu}t} \right]$$

where the amplitudes  $\overline{E}(\omega_{\mu}, t)$  and  $\overline{P}(\omega_{\mu}, t)$  are slowly varying functions of t. The rate of change of the material energy density is given by

$$\frac{\partial \mathcal{U}}{\partial t} = 2\operatorname{Re} \sum_{\nu=1}^{n} \left[ \overline{E}^{*}(\omega_{\nu}, t) \cdot \frac{\partial \overline{P}(\omega_{\nu}, t)}{\partial t} + i \omega_{\nu} \overline{E}^{*}(\omega_{\nu}, t) \cdot \overline{P}(\omega_{\nu}, t) \right]$$

+ high frequency terms.

Taking a time average over an interval T long compared to  $\frac{1}{\omega_{\nu}}$  but short compared to the time for the amplitudes  $\overline{E}(\omega_{\nu}, t)$  and  $\overline{P}(\omega_{\nu}, t)$  to change appreciably, the high frequency terms will drop out and the time average rate of change of material energy density is

$$\frac{\partial U}{\partial t} = 2\operatorname{Re} \sum_{\nu=1}^{n} \left[ \overline{E}^{*}(\omega_{\nu}, t) \cdot \frac{\partial \overline{P}(\omega_{\nu}, t)}{\partial t} + i\omega_{\nu}\overline{E}^{*}(\omega_{\nu}, t) \cdot \overline{P}(\omega_{\nu}, t) \right].$$

For a nondissipative media, the time average work done on the medium is zero after the fields have reached a steady state value (i.e.  $\frac{\partial \bar{P}(\omega_{\nu}, t)}{\partial t} = 0$ ). Thus

$$\left\langle \frac{\partial U}{\partial t} \right\rangle_{\substack{\text{steady} \\ \text{state}}} = 2\text{Re} \sum_{\nu=1}^{n} i\omega_{\nu} \bar{E}^{*}(\omega_{\nu})^{*} \bar{P}(\omega_{\nu}) = 0. \quad (2-17)$$

This equation is just a statement that the total power flow is a constant, even though it may redistribute itself among the various frequencies. When the fields are initially turned on, work must be done on or by the medium to establish the steady state value of the polarization.

In the nonsteady state, the field at frequency  $\omega_{\nu}$  is slowly changing in time, so it is not strictly monochromatic until it reaches its steady state value. However, the polarization  $\bar{P}(\omega_{\nu}, t)$  can still be taken as a function of the field amplitude  $\bar{E}(\omega_{\nu}, t)$  if the dispersion is low. In the case of a linear polarization, the requirement is  $\frac{\partial \in (\omega)}{\partial \omega} << \frac{e}{\omega}$  [see Bloembergen (16)]. With this restriction and the assumption that equation (2-17) holds even in the nonsteady state, the time average rate of change of material energy density in the nonsteady state becomes

$$\left\langle \frac{\partial U}{\partial t} \right\rangle_{\substack{\text{nonsteady}\\\text{state}}} = \frac{d \overline{\Phi}}{d t} = 2 \operatorname{Re} \Sigma \overline{E}^*(\omega_{\nu}, t) \cdot \frac{\partial \overline{P}(\omega_{\nu}, t)}{\partial t} \cdot \frac{\partial \overline{P$$

The function  $\oint$  represents the average energy required to polarize the medium. It would seem physically reasonable to argue that this average energy  $\oint$  should only depend on the final state of the medium and not on the path by which the final state was reached. This requires  $\oint$  to be a perfect differential i.e.

$$d \vec{\Phi} = 2 \operatorname{Re} \Sigma \vec{E}^* (\omega_{\nu}, t) \vec{P} (\omega_{\nu}, t).$$

Define a new function

$$F = \oint - 2\operatorname{Re} \Sigma \quad \mathbb{E}^{*}(\omega_{j}, t) \quad \mathbb{P}(\omega_{j}, t).$$

$$\gamma = 1$$

The second term is the energy density of the polarization in the field. Hence the function F is associated with the work done by the generators in order to establish the fields in the presence of the medium and can be identified with the Helmhotz free energy. Its total differential is

$$dF = -2Re \Sigma \vec{P} (\omega_{j}, t) d\vec{E}^{*} (\omega_{j}, t)$$

$$\nu = 1$$

Returning to the more general case with magnetic and electric quadrupole polarizations, the total differential of F is

$$dF = -2Re \sum_{\nu=1}^{n} \left[ \bar{P}(\omega_{\nu}, t) d\bar{E}^{*}(\omega_{\nu}, t) + \bar{M}(\omega_{\nu}, t) d\bar{H}^{*}(\omega_{\nu}, t) \right]$$

$$+ \bar{Q}(\omega_{\nu}, t) d: \left\{ \bar{\nabla} \bar{E}^{*}(\omega_{\nu}, t) \right\}$$
(2-18)

Hence

$$\bar{P}(\omega_{\mu},t) = -\frac{\partial F}{\partial \bar{E}^{*}(\omega_{\mu},t)}$$

$$\bar{H}(\omega_{\mu},t) = -\frac{\partial F}{\partial \bar{H}^{*}(\omega_{\mu},t)}$$
(2-19)

$$\bar{Q}(\omega_{\nu},t) = -\frac{\partial F}{\partial \nabla \bar{E}^{*}(\omega_{\nu},t)}$$

and there does exist a time average free energy F from which the moments  $\bar{\mathbf{P}}$ .  $\bar{\mathbf{M}}$ , and  $\bar{\mathbf{Q}}$  can be derived. Pershan (25) has given evidence that the

time averaged free energy probably exists under conditions more general than have been proven here.

In general, the function F will depend on the amplitudes  $\overline{E}_{,}$   $\overline{E}^{*}$ ,  $\overline{H}$ ,  $\overline{H}^{*}$ ,  $\overline{\nabla}\overline{E}_{,}$  and  $\overline{\nabla}\overline{E}^{*}$ . As with the polarization, the procedure now is to expand the free energy F in terms of these quantities. Each term in the expansion must be independent of time, so that the sum of the frequencies associated with the starred amplitudes must be equal to the sum of the frequencies associated with the unstarred amplitudes. Thus, for example,  $\mathcal{X}\overline{E}^{*}(2\omega)\overline{E}(\omega)\overline{E}(\omega)$  is an allowed term but  $\mathcal{X}\overline{E}(2\omega)\overline{E}^{*}(\omega)E(\omega)$ is not.

From the various terms in the expansion of the free energy, the different linear and nonlinear effects can be described. For example, linear effects are derived from a free energy  $F = -2\text{Re}\left[\mathcal{X}:\bar{E}^*(\omega)\bar{E}(\omega)\right]$ while optical activity can be obtained from either  $F = -2\text{Re}\left[\mathcal{X}:\bar{E}^*(\omega)\bar{E}(\omega)\right]$  $\bar{E}^*(\omega)\bar{\nabla}\bar{E}(\omega)$  or  $F = -2\text{Re}\left[\mathcal{X}:\bar{E}^*(\omega)\bar{H}(\omega)\right]$ . An account of the various effects which follow from the different terms in the expansion of the free energy can be found in an article by Pershan (26). In this thesis, the interest will be in only those terms which will produce frequency doubling, i.e. those terms containing three fields.

When non-zero, the dominant term for frequency doubling is the electric dipole. It can be derived from a free energy proportional to three electric fields, i.e.  $F = -2Re\left[\chi:\bar{E}^*(2\omega)\bar{E}(\omega)\bar{E}(\omega)\right]$ . For the present, let the three fields have different frequencies  $\omega_3$ ,  $\omega_2$ , and  $\omega_1$  where  $\omega_3 = \omega_2 + \omega_1$ . Then,

$$F = - \left[ \chi_{ijk}(\omega_3, \omega_2, \omega_1) E_i^*(\omega_3) E_j(\omega_2) E_k(\omega_1) \right] \\ + \chi_{ijk}^*(\omega_3, \omega_2, \omega_1) E_i^*(\omega_3) E_j^*(\omega_2) E_k^*(\omega_1) \right],$$

Using equation (2-19) the induced polarizations at these frequencies are

$$P_{i}(\omega_{3}) = \chi_{ijk}(\omega_{3}, \omega_{2}, \omega_{1}) E_{j}(\omega_{2}) E_{k}(\omega_{1})$$

$$P_{j}(\omega_{2}) = \chi_{ijk}^{*}(\omega_{3}, \omega_{2}, \omega_{1}) E_{i}(\omega_{3}) E_{k}^{*}(\omega_{1})$$

$$P_{k}(\omega_{1}) = \chi_{ijk}^{*}(\omega_{3}, \omega_{2}, \omega_{1}) E_{i}(\omega_{3}) E_{j}^{*}(\omega_{2}).$$

Pershan (26) has shown that for a lossless nonmagnetic material the susceptibilities  $\mathcal{X}_{ijk}(\omega_3, \omega_2, \omega_1)$  are real. By definition the induced polarizations at the three frequencies are

$$P_{i}(\omega_{3}) \equiv \chi_{ijk}(\omega_{3}, \omega_{2}, \omega_{1})E_{j}(\omega_{2})E_{k}(\omega_{1})$$

$$P_{j}(\omega_{2}) \equiv \chi_{jik}(\omega_{2}, \omega_{3}, \omega_{1})E_{i}(\omega_{3})E_{k}^{*}(\omega_{1})$$

$$P_{k}(\omega_{1}) \equiv \chi_{kij}(\omega_{1}, \omega_{3}, \omega_{2})E_{i}(\omega_{3})E_{k}^{*}(\omega_{1}).$$

A comparison of these with the three previous equations shows that

$$\mathcal{X}_{\mathtt{j}\mathtt{k}}(\omega_3,\omega_2,\omega_1)=\mathcal{X}_{\mathtt{j}\mathtt{i}\mathtt{k}}(\omega_2,\omega_3,\omega_1)=\mathcal{X}_{\mathtt{k}\mathtt{i}\mathtt{j}}(\omega_1,\omega_3,\omega_2)$$

These are the permutation symmetry relations first derived by Armstrong <u>et al</u>. (14) from perturbation theory. They state that equivalent susceptibilities can be formed by permuting the indices provided that the frequencies associated with each are also interchanged. For example, if  $\omega_1 = -\omega$ ,  $\omega_2 = \omega$ , then  $\omega_3 = 0$  and  $\chi_{ijk}(0, \omega, -\omega) =$   $\chi_{jik}(\omega, 0, -\omega)$ ; the susceptibilities that describe optical rectification are related to those of the electro-optic effect.

Reverting to frequency doubling  $(\omega_1 = \omega_2 = \omega, \text{ and } \omega_3 = 2\omega)$ , for a lossless nonmagnetic material

$$\mathbf{F} = - {}^{\mathbf{P}} \chi_{\mathbf{ijk}}^{\mathbf{EE}}(2\omega, \omega, \omega) \left[ \mathbf{E}_{\mathbf{i}}^{*}(2\omega) \mathbf{E}_{\mathbf{j}}(\omega) \mathbf{E}_{\mathbf{k}}(\omega) + \mathbf{E}_{\mathbf{i}}(2\omega) \mathbf{E}_{\mathbf{j}}^{*}(\omega) \mathbf{E}_{\mathbf{k}}^{*}(\omega) \right] .$$

Using equation (2-19)

$$P_{i}(2\omega) = {}^{P}\chi_{ijk}^{EE}(2\omega,\omega,\omega) E_{j}(\omega)E_{k}(\omega)$$

$$P_{j}(\omega) = {}^{P}\chi_{ijk}^{EE}(2\omega,\omega,\omega) E_{i}(2\omega)E_{k}^{*}(\omega)$$

$$P_{k}(\omega) = {}^{P}\chi_{ijk}^{EE}(2\omega,\omega,\omega) E_{i}(2\omega)E_{j}^{*}(\omega).$$

As shown in section (2-1) the susceptibility  ${}^{P}\chi_{ijk}^{EE}(2\omega,\omega,\omega)$  is symmetric in its last two indices and must satisfy the requirements of crystal symmetry. In addition, permutation symmetry relates the susceptibilities for frequency doubling with those for difference-frequency mixing of a wave at frequency 2 $\omega$  with one at $\omega$ .

The permutation symmetry relations are a generalization of Kleinman's symmetry condition (27).

 $\chi_{\mathbf{i}\mathbf{j}\mathbf{k}}(\omega_3,\omega_2,\omega_1)=\chi_{\mathbf{j}\mathbf{i}\mathbf{k}}(\omega_3,\omega_2,\omega_1)=\chi_{\mathbf{k}\mathbf{i}\mathbf{j}}(\omega_3,\omega_2,\omega_1),$ 

in which the indices may be permuted without regard to frequencies. This condition is valid if the origin of the frequency doubling is a dispersionless mechanism in which the susceptibilities do not depend on frequency. Hence

 $\chi_{\mathbf{ijk}^{\mathrm{E}}\mathbf{i}^{*}(2\omega)\mathbb{E}_{\mathbf{j}}(\omega)\mathbb{E}_{\mathbf{k}}(\omega)} = \chi_{\mathbf{jik}^{\mathrm{E}}\mathbf{j}}(\omega)\mathbb{E}_{\mathbf{i}^{*}(2\omega)\mathbb{E}_{\mathbf{k}}(\omega)}$ 

=  $\chi_{kijk} (\omega) E_i (2\omega) E_j (\omega)$  resulting in the above relations.

In the case of second harmonic generation, this additional symmetry reduces the number of independent coefficients from 18 to 10 in the most general case of a triclinic crystal. Experimentally, the validity of the symmetry condition has been tested in many different materials (28,29,30), and within the limits of experimental error it has been satisfied in every one. These results are significant in that they indicate a high frequency electronic mechanism as the origin of the frequency doubling.

Electric quadrupole frequency doubling will be considered next. It is derivable from

$$F = -2\operatorname{Re}\left[{}^{\operatorname{P}}\chi_{ijkl}^{\operatorname{E}\nabla E}(2\omega,\omega,\omega) E_{i}^{*}(2\omega) E_{j}(\omega) \partial_{k}E_{l}(\omega) + \frac{Q}{\chi_{ljki}^{\operatorname{E}E}(\omega,\omega,2\omega) E_{l}(\omega) E_{j}(\omega) \partial_{k}E_{i}^{*}(2\omega)\right] . \quad (2-20)$$

Note that there are two different susceptibilities because there are two kinds of products  $\overline{E}^*(2\omega)\overline{E}(\omega) \overline{\nabla} \overline{E}(\omega)$  and  $\overline{E}(\omega)\overline{E}(\omega) \overline{\nabla} \overline{E}^*(2\omega)$ . For a lossless nonmagnetic material the susceptibilities are real. They are also symmetric in the last two indices;

$${}^{P}\chi_{ijkl}^{EVE}(2\omega,\omega,\omega) = {}^{P}\chi_{ijlk}^{EVE}(2\omega,\omega,\omega)$$
 and

$$\begin{split} & \mathcal{X}_{ljki}^{\text{EE}}(\omega,\omega,2\omega) = \mathcal{X}_{ljik}^{\text{EE}}(\omega,\omega,2\omega), \text{ since the antisymmetric} \\ & \text{part is accounted for by magnetic dipole effects which will be discussed} \\ & \text{later. Permutation symmetry requires } \mathcal{X}_{ljki}^{\text{EE}}(\omega,\omega,2\omega) = \mathcal{X}_{jlki}^{\text{EE}}(\omega,\omega,2\omega) \\ & \text{and } \mathcal{X}_{ijkl}^{\text{EVE}}(2\omega,\omega,\omega) = \mathcal{X}_{jikl}^{\text{EVE}}(\omega,2\omega,\omega). \end{split}$$

Using equation (2-19) again and the free energy in (2-20), the induced moments at the doubled frequency are

$$P_{i}(2\omega) = {}^{P}\chi_{ijk}^{EVE}(2\omega,\omega,\omega)E_{j}(\omega)\partial_{k}E_{\ell}(\omega)$$
$$Q_{ki}(2\omega) = {}^{Q}\chi_{\ell jki}^{EE}(\omega,\omega,2\omega)E_{\ell}(\omega)E_{j}(\omega).$$

With these the induced source current  $\overline{J}$  at the doubled frequency is

$$J_{i}(2\omega) = \frac{\partial}{\partial t} \left[ P_{i}(2\omega) - \partial_{k} Q_{ki}(2\omega) \right].$$

Pershan (26) has shown that the source current derived from the free energy F in (2-20) and the free energy F' = F  $\neq \nabla \cdot G$  where  $\nabla \cdot G$ =  $\partial_k \left[ Y_{kij\ell} (2\omega, \omega, \omega) E_i^* (2\omega) E_j(\omega) E_\ell(\omega) \right]$  are the same. It is possible, therefore, with no loss in generality to set one of the tensors, say  $P_{ijk\ell}^{EVE} (2\omega, \omega, \omega)$ , equal to zero. Quadrupole effects are now derivable from

$$\mathbf{F} = -2\operatorname{Re} \, \overset{\mathrm{Q}}{\mathbf{\chi}}_{ijkl}^{\mathrm{EE}}(\omega, \omega, 2\omega) \, \operatorname{E}_{i}(\omega) \, \operatorname{E}_{j}(\omega) \, \nabla_{k} \operatorname{E}_{l}^{*}(2\omega)$$

and

$$Q_{kl}(2\omega) = Q_{ijkl} E_{i}(\omega) E_{j}(\omega)$$
(2-21)

The last type of frequency doubling that will be considered in detail is the magnetic dipole. It can be equivalent in magnitude to the electric quadrupole. The induced moments at the doubled frequency are obtained from

$$\mathbf{F} = -2\operatorname{Re}\left[ {}^{\operatorname{P}}\chi_{\mathbf{i}\mathbf{j}\mathbf{k}}^{\operatorname{EH}}(2\omega,\omega,\omega) \operatorname{E}_{\mathbf{i}}^{*}(2\omega) \operatorname{E}_{\mathbf{j}}(\omega) \operatorname{H}_{\mathbf{k}}(\omega) \right. \\ \left. + {}^{\operatorname{M}}\chi_{\mathbf{k}\mathbf{j}\mathbf{i}}^{\operatorname{EE}}(\omega,\omega,2\omega) \operatorname{E}_{\mathbf{k}}(\omega) \operatorname{E}_{\mathbf{j}}(\omega) \operatorname{H}_{\mathbf{i}}^{*}(2\omega) \right] . \quad (2-22)$$

Like the electric quadrupole effects, there are two different susceptibilities in the free energy since there are two kinds of products. However,  ${}^{P}\chi_{ijk}^{EH}$  and  ${}^{M}\chi_{kji}^{EE}$  are third order axial tensors which are pure imaginary in a lossless nonmagnetic material. Also, permutation symmetry requires

$${}^{M}\chi_{kji}^{EE}(\omega,\omega,2\omega) = {}^{M}\chi_{jki}^{EE}(\omega,\omega,2\omega) \text{ and}$$

$${}^{P}\chi_{ijk}^{EH}(2\omega,\omega,\omega) = {}^{P}\chi_{jik}^{EH}(\omega,2\omega,\omega).$$

The induced moments are

$$P_{i}(2\omega) = {}^{P}\chi_{ijk}^{EH}(2\omega,\omega,\omega) E_{j}(\omega) H_{k}(\omega)$$

$$(2-23)$$

$$M_{i}(2\omega) = {}^{M}\chi_{kji}^{EE}(\omega,\omega,2\omega) E_{k}(\omega) E_{j}(\omega)$$

and the frequency doubling source current is

$$\overline{\mathbf{J}}(2\,\omega) = \frac{\partial \overline{\mathbf{P}}(2\,\omega)}{\partial t} + c \,\overline{\nabla} \mathbf{x} \,\overline{\mathbf{M}}(2\,\omega).$$

Unlike electric dipole frequency doubling, both magnetic dipole and electric quadrupole frequency doubling are possible in a crystal with a centre of symmetry.

There are other terms in the free energy which can produce frequency doubling such as  $F = \chi E HVE$ , or  $\chi EVEVE$ , etc., but they all contain higher powers of  $\nabla E$  and H so the effects they describe will be smaller than those that have been listed here.

### (2-5) The Azimuthal Dependence of Frequency Doubling in Crystals

A simple frequency doubling experiment that can be performed in uniaxial crystals, is to measure the amount of second harmonic at phase matching as the crystal is rotated about the optic axis. The dependence of the frequency doubling on the azimuthal angle  $\phi$  may cast light on the type of nonlinearity that is involved since different tensors may lead to different functional forms.

The object of this section is to show how the magnitude of the frequency doubling depends on the angle  $\not o$ . In particular, the azimuthal dependence of the electric dipole frequency doubling in a uniaxial negative crystal will be determined. In the following, the applied fields are assumed to be plane waves propagating through the crystal in the phase matched direction  $\bar{n}$  where

$$\bar{n} = \begin{bmatrix} \sin \theta \cos \phi \\ \sin \theta \sin \phi \\ \cos \theta \end{bmatrix}$$

The optic axis has been taken in the z axis direction. The angle  $\theta$  is measured from the optic axis to the direction of propagation, while  $\phi$  is the angle between the crystallographic x axis and the principal plane. The O-ray fields will be written

 $\overline{E}^{\circ}(\omega) = \overline{o} E^{\circ} e^{i(\overline{k}^{\circ} \cdot \overline{r} - \omega t)} \overline{H}^{\circ}(\omega) = \overline{h}^{\circ} H^{\circ} e^{i(\overline{k}^{\circ} \cdot \overline{r} - \omega t)}$ 

where

$$\bar{\mathbf{o}} = \begin{bmatrix} \sin\phi \\ -\cos\phi \\ \mathbf{o} \end{bmatrix} \qquad \bar{\mathbf{h}}^{\circ} = \begin{bmatrix} \cos\theta\cos\phi \\ \cos\theta\sin\phi \\ -\sin\theta \end{bmatrix}$$

and the E-ray as

$$\overline{E}^{e}(\omega) = \overline{e}_{1} E^{e} e^{i(\overline{k}^{e} \cdot \overline{r} - \omega t)}, \quad \overline{H}^{e}(\omega) = \overline{h}^{e} H^{e} e^{i(\overline{k}^{e} \cdot \overline{r} - \omega t)}$$

where

$$\bar{\mathbf{e}}_{1} = \begin{bmatrix} -\cos(\theta + \alpha_{1}) \cos\phi \\ -\cos(\theta + \alpha_{1}) \sin\phi \\ \sin(\theta + \alpha_{1}) \end{bmatrix} \qquad \bar{\mathbf{h}}^{e} = \begin{bmatrix} \sin\phi \\ -\cos\phi \\ \mathbf{o} \end{bmatrix}$$

The quantity  $\alpha_1$  is the angle between the direction of Poynting's vector for the E-ray and its wave normal  $\overline{k}^e$ . It appears in  $\overline{e}_1$  because the electric field is not necessarily perpendicular to the wave normal in a crystalline medium. The magnitude of  $\alpha_1$  can be obtained

from

$$\tan \alpha_{1} = \frac{\left(1 - \frac{n_{1}}{n_{1}}e^{2}\right) \tan \theta}{1 + \frac{n_{1}}{n_{1}}e^{2}} \tan^{2}\theta}$$

In general, the total fields in the crystal are superpositions of the E- and O-ray fields. Therefore

$$E_{j}(\omega) = o_{j} E^{e} e^{i(\vec{k}^{e} \cdot \vec{r} - \omega t)} + e_{lj} E^{e} e^{i(\vec{k}^{e} \cdot \vec{r} - \omega t)}$$

with an analogous expression for  $H_j(\omega)$ . As this field propagates through the medium, an electric dipole polarization,

$$P_{i}(2\omega) = {}^{P}\chi_{ijk}^{EE} E_{j}(\omega) E_{k}(\omega)$$

is induced where

$$E_{j}(\omega) E_{k}(\omega) = o_{j}o_{k} E^{o^{2}} e^{2i(\vec{k}^{o}\cdot\vec{r}-\omega t)}$$

$$+ (o_{j}e_{lk} + e_{lj}o_{k}) E^{o} E^{e} e^{i(\vec{k}^{o} + \vec{k}^{e})\cdot\vec{r}-2\omega t)}$$

$$+ e_{lj}e_{lk} E^{e^{2}} e^{2i(\vec{k}^{e}\cdot\vec{r}-\omega t)} .$$

For OO-E phase matching only the first term in  $E_j(\omega) E_k(\omega)$  need be considered. On the other hand, the second term may lead to OE-E type phase matching. The last term is never effective in uniaxial negative crystals, but would lead to EE-O phase matching in a suitable positive crystal. An OE-O type phase matching is also possible in positive crystals. Only OO-E phase matching in uniaxial negative crystals will be considered in the following, but the azimuthal dependence in the other cases can be obtained in a similar manner.

The induced polarization

$$P_{i}(2\omega) = {}^{P}\chi_{ijk}^{EE} \circ_{j} \circ_{k} E^{\circ 2} e^{2i(\vec{k}^{\circ}\cdot\vec{r} - \omega t)}$$

will produce a source current,  $\overline{J} = \frac{\partial \overline{P}}{\partial t} = -2i\omega \overline{P}(2\omega)$ , at the doubled frequency. Not all the current is effective in producing doubled frequency, but only that component in the direction  $\overline{e}_2$  of the E-ray electric field at the doubled frequency where

$$\bar{e}_{2} = \begin{bmatrix} -\cos(\theta + \alpha_{2})\cos\phi \\ -\cos(\theta + \alpha_{2})\sin\phi \\ \sin(\theta + \alpha_{2}) \end{bmatrix}$$

and  $\alpha_2$  is given by

$$\tan \alpha_2 = \frac{\begin{pmatrix} n_2^{\circ^2} \\ 1 - \frac{n_2^{\circ^2}}{n_2^{\circ^2}} \end{pmatrix}}{1 + \frac{n_2^{\circ^2}}{n_2^{\circ^2}}} \tan^{\theta}$$

The angles  $\alpha_1$  and  $\alpha_2$  are not necessarily the same because of dispersion. The effective source current is

$$J_{\text{eff}} = \bar{e}_{2} \cdot \bar{J} = -2i \omega e_{2i} P_{i}(2\omega)$$
$$= -2i \omega E^{2} \bar{\Phi} e^{2i} (\bar{k}^{\circ} \cdot \bar{r} - \omega t)$$

where the azimuthal dependence is contained in the quantity  $\oint = e_{2i}^{P}\chi_{ijk}^{EE} \circ_{j} \circ_{k}$ . Since the amplitude of the second harmonic is proportional to the magnitude of  $J_{eff}$ , the intensity of the second harmonic will be proportional to  $\oint^{2}$ . In general  $\oint$  consists of the sum of 27 terms each one being the product of the third order polar tensor  ${}^{P}\chi_{ijk}^{EE}$  and the quantity  $e_{2i} \circ_{j} \circ_{k}$ . Particularizing to the case of KDP which has only three nonzero coefficients,  ${}^{P}\chi_{123}^{EE}$ ,  ${}^{P}\chi_{213}^{EE}$ , and  ${}^{P}\chi_{312}^{EE}$  the sum becomes

where  $\theta$  is the OO-E phase matching angle. The second harmonic intensity in KDP should have a  $\sin^2 2\phi$  dependence with the maximum doubled frequency being produced at the azimuthal angle  $\phi = 45^\circ$ . This aximuthal dependence has been observed by Maker et al. (3).

In the Appendix, the azimuthal dependence of the electric dipole, magnetic dipole, and electric quadrupole frequency doubling is calculated for both OO-E and OE-E type phase matching. The functional dependences for the point groups of the tetragonal, trigonal and hexagonal crystal systems are given. The results, however, are only applicable to uniaxial negative crystals.

#### CHAPTER III

#### EXPERIMENTAL APPARATUS AND PROCEDURE

# (3-1) Introduction

The objective of experiments in frequency doubling is to detect the low intensity doubled frequency that is generated when a powerful monochromatic light beam is transmitted through a nonlinear crystal. The source of highly intense light is usually provided by a Q-spoiled The principle of this device is described in the literature laser. (31, 32, 33). After the laser light passes through the nonlinear crystal, the light beam contains both the laser frequency and its second harmonic. This doubled frequency can be separated from its fundamental by two different means. In the first method, the light is focused on the slit of a prism spectrograph and the second harmonic light is refracted out of the laser light and focused on a slit in front of a detector. A grating can be used instead of a prism but care must be taken to use orders which do not overlap at the fundamental and doubled frequencies. In the second method the light beam is passed through a filter which transmits only the doubled frequency. In both cases a photomultiplier is used to detect the intensity of the second harmonic. By inserting a beam splitter into the path of the laser beam in front of the nonlinear crystal the intensity of the fundamental frequency used to generate the second harmonic can be measured, or at least monitored. The following

sections give a detailed description of the experimental apparatus and procedures which were used in this investigation.

## (3-2) Construction and Operation of the Q-spoiled Laser

The principles of operation of a Q-spoiled laser were first proposed by Hellworth (31). He suggested that an ordinary laser can be made to emit a short burst of highly intense light if the losses in the laser cavity are controlled so that they are high during the pumping period until a high inversion is obtained, at which point the losses are switched to a low value. When a laser is operated in this mode it is called Q-spoiling, since the quality factor of the cavity is kept at a low value, i.e. spoiled, until at an appropriate moment the cavity Q is switched to a high value.

In this work, it was decided to accomplish the Q-switching with a rotating prism. A Kerr cell was considered, but not adopted because operation in the infrared was desired. Hence a Beckman & Whitley (Technical Operations Inc.) model 402 rotating prism laser Q-spoiler was purchased. The prism angles are 90°, 45°, and 45°. Such a prism has the property that, after two total internal reflections, light rays are deviated through 180° regardless of the angle of incidence. When the prism is substituted in place of one of the reflectors of the laser cavity and aligned so that its roof edge is parallel to the other reflector, a new laser cavity is formed. Since light rays are now reflected twice through the crystal in one pass through the laser cavity, the cavity length is approximately twice the distance between the reflector and the prism. Due to the reflection properties of the roof prism, the alignment of the hypotenuse face with the other cavity reflector is not critical. In the Beckman & Whitley Q-spoiler, the prism is mounted on a shaft with the hypotenuse face parallel to the shaft and the roof edge perpendicular to the shaft. It is designed to be driven by compressed air. With the aid of a regulator valve, the air pressure supplied to the Q-spoiler could be varied from 0 to 70 lb/in<sup>2</sup> and hence the rotational speed of the prism could be controlled from 0 to 1500 revolutions per sec (rps). At the top of the Q-spoiler a magnetic pick-up coil is mounted, which produces a sinusodal signal whose frequency is equal to the rotational rate of the prism. By feeding this signal to a frequency counter, the rotational speed of the prism can be measured. During a typical experiment when the prism was operating at a rotational speed of approximately 450 rps, the actual rotational rate could drift by as much as 30 rps over a period of 20 minutes. However, by making appropriate adjustments in the air pressure when necessary, the rotor speed could be held to within 5 rps of a mean value.

Since the optimum time during the pumping period when the prism should be aligned is less than 100µs in duration, it is necessary to synchronize the operation of the flashtube with the rotating prism. This was accomplished by constructing a rotor-flashtube synchronizing unit. The sinusodal output from the Q-spoiler is converted into a train of short duration pulses using a multivibrator. The interval between the pulses corresponds to the period of revolution of the prism and each pulse has a definite phase relationship with respect to the instant of prism alignment. This phase can be controlled by adjusting the pick-up coil on top of the Q-spoiler. It was set so that alignment occurred about 300µs after each multivibrator pulse. After a switch on the synchronizing unit is closed, the first multivibrator pulse triggers a thyratron which in turn triggers the power supply which operates the flashtube. The triggering of the flashtube occurs almost instantaneously with the multivibrator pulse. Since the light output from the flashtube takes about 200µs to reach a maximum, the rotor comes into alignment at the appropriate time.

The Q-spoiled laser that was constructed could be operated with either a ruby laser crystal or a neodymium (Nd) doped laser crystal. The output of the ruby laser occurs at .6943µm while that of the Nd laser is at 1.06µm. In general, because of the longer wavelength, velocity matching in frequency doubling experiments with a Nd laser is possible in more nonlinear crystals than with a ruby laser. The reason is that dispersion between 1.06µm and .53µm is usually less than that between .6943µm and .3472µm and hence the nonlinear crystal does not require as much birefringence. Since the nonlinear crystal should be transparent at both the fundamental and doubled frequency, this factor must also be considered in choosing the type of laser that is used.

The ruby crystals  $(Cr^{3+}:Al_2O_3)$  were purchased from Adolf Meller Co. They are cylindrical rods 0.25 inches in diameter and 2.0 inches long with the ends ground flat to  $\lambda/4$  (sodium light) and parallel to within  $\pm 6$  seconds of arc. The crystals were grown from a melt that had a doping of 0.04% chromium oxide  $(Cr_2O_3)$  by weight in aluminium oxide  $(Al_2O_3)$ . Two types of Nd laser crystals, a neodymium doped calcium tungstate  $(Nd^{3+}:CaWO_4)$  and a neodymium doped glass, were purchased. Like the ruby crystal, the Nd<sup>3+</sup>:CaWO<sub>4</sub> crystal was purchased from Adolf

Meller Co. It has a doping of 5% neodymium oxide  $(Nd_2O_2)$  by weight in  $CaWO_{L}$  and the other specifications are the same as quoted above. The Nd-glass laser crystals were purchased from Eastman Kodak Co. and are of the type ND-11. They are not crystals in the real sense but rather a 1 to 3% doping of neodymium oxide in a silicate optical glass. For Q-spoiling experiments, this type of crystal is to be preferred over the type ND-10 (also manufactured by Eastman Kodak Co.) which is a doped barium crown glass. The reason is that the life time of the metastable level in Nd<sup>3+</sup> is longer in ND-11 ( $\sim$ 360µs) than in ND-10 ( $\sim$ 50µs). Hence with a given optical pumping system, a greater inversion can be obtained with ND-11. The Nd-glass crystals purchased for this work were 0.25 inches in diameter by 3.0 inches long with the ends flat to  $\lambda/10$  and parallel to within  $\pm 6$  seconds of arc. Since these crystals were to be used exclusively in a Q-spoiled laser they were purchased with antireflection coatings on each end.

If a Nd-glass laser crystal is exposed directly to the light from the flashtube, the crystal will darken after a large number of flashes and its threshold for oscillation increases. Eastman Kodak<sup>†</sup> calls this darkening "solarization" and attributes it to ultra-violet in the pump light. It was found that the life of a crystal before the onset of solarization could be extended from 50 to well over 500 flashes by surrounding the glass crystal with an ultra-violet filter. In these experiments an amber glass filter code 3555 manufactured by Corning Glass Works was used.

<sup>†</sup> That company now claims to have eliminated the problem of solarization in its newer Nd-glass laser crystals.

To optically pump the laser crystal an elliptical laser head was constructed. The purpose of an optical pumping system is to convert as efficiently as possible the light from the flashtube into excited atoms in the crystal. How effectively this is accomplished depends on the degree of light concentration on the crystal and absorption of this light in the crystal. The elliptical cylinder type reflector that was constructed has the property that light emitted from a linear flashtube situated along one focus of the ellipse is imaged on a laser crystal at the other focus. For a flashtube of finite diameter, the magnification of its image at the laser crystal is least when the foci are closest together. Hence the greatest efficiency for concentrating light on the crystal is obtained when the eccentricity of the ellipse is as small as is practical. It is also advantageous to use a crystal which is at least as large in diameter as the flashtube. Within a limited area. this pumping system is capable of a one to one transformation of the pumping light density from the flashtube to the laser crystal. Unfortunately since most of the transmitted light is refracted on passing through the crystal, it is lost and only the light absorbed in a single pass through the crystal is useful for atomic excitation. Nevertheless, the constructed elliptical laser head was found to be four times more effective than a previously built cylindrical laser head using a helical flashtube as a pump source. An even more efficient optical pumping geometry has been proposed and built by Roess (34). His reflector is an ellipsoid of revolution with the axis of the linear flashtube mounted along the axis of the ellipsoid between the surface of the reflector and the nearest focus. The crystal is similarly mounted

between the reflector wall and the other focus. Although the source no longer forms an actual image in the laser crystal, this reflector design still has the high efficiency of light concentration of the elliptical cylinder reflector with the added benefit of increased light absorption due to the possibility of multiple reflection of the pump light many times through the laser crystal.

The fabrication of the elliptical laser head was accomplished by following some of the techniques of Hronik et al. (35). Elliptical forms were cut by boring vertically through 0.5 inch thick aluminium plates with the axis of rotation of the circular milling cutter slanted at an angle of 22 degrees to the vertical. Each form so cut is in the shape of one half of an ellipse divided along the line connecting its foci. The length of the major axis is determined by the diameter of the milling cutter (4 inches) and the length of the minor axis depends also on the angle at which the milling cutter is set. Six elliptical forms were cut in one operation and drilled with holes in which aligning pins could be inserted. Three of the forms were then assembled with appropriate spacers to make each half of an elliptical cylinder rib cage 3.5 inches long. The reflecting surface of the laser head was formed by pressing .020 inch thick polished aluminium sheet into the form and fastening it with epoxy. With the addition of flat polished aluminium end plates, the reflector was completed. A photograph of the top half of the laser head is shown in Figure 3 and Figure 4 is a schematic diagram of the bottom half. The semi-major axis is 1.98 inches and the semi-minor axis 1.83 inches, giving an eccentricity of 0.4 and a distance between foci of 1.5 inches. This method of construction has the

Figure 3.

Photograph of Top Half of Elliptical Reflector



Figure 4.

Schematic Diagram of Bottom Half of Laser Head



advantage that the reflecting surface can be polished while it is flat. Furthermore, the completed laser head separates into two halves, allowing ready access to the flashtube and the crystal. With the top half of the reflector off, it is easy to align the bottom half so that the flashtube and the crystal are along the foci of the ellipse. This is done by confirming that the image of the crystal in the reflector is located at the flashtube.

The laser crystal is excited by an Edgerton, Germeshausen, & Grier FX42 linear xenon flashtube. As is shown in Figure 4, the flashtube is mounted on the bottom half of the laser head. Provision was made to pass air from a blower over the flashtube to cool it. The laser crystal is held at the other focus by supports which are independent of the reflector. Both the elliptical reflector and the crystal holder are fastened to a thick metal plate and attached to a lathe bed.

A commercial power supply and capacitor bank purchased from GNB Inc. were used to provide the stored energy and the pulse for initiating the flashtube. The flashtube can be fired manually or with an external trigger. In either case, a 20 kilovolt pulse from the power supply applied to the flashtube ionizes the xenon gas and the stored energy in the capacitor bank discharges through the flashtube. A 100 millihenry inductance is connected in series to limit the discharge current and hence extend the life of the flashtube. The light pulse is about 0.5 millisec. in duration with the peak output occurring 0.2 millisec. after the flashtube is initiated. The rated maximum energy that can be discharged through the flashtube is 600 joules. When the laser is operated in the Q-spoiled mode, the external trigger pulse for the power supply is supplied by the rotor-flashtube synchronizing unit.

The construction of the Q-spoiled laser was completed with the addition of the output reflector to the laser cavity. In initial experiments, a partially transmitting silver coating was evaporated on one end of the laser crystal. However, it was found that this deteriorated quite rapidly. In fact, when the laser was operated in the Q-spoiled mode, more than half of the silvering could be lost in a single flash. The difficulty was eliminated by using a resonant reflector manufactured by Lear Siegler Inc. These reflectors constructed of plane parallel sapphire platelets, operate on the principle that there is a reflected wave from any index of refraction discontinuity. Furthermore, the reflectivity from a transparent platelet can be high for those wavelengths called the resonant wavelengths, for which the reflected light from the first surface adds in amplitude with that from the second surface. The reflectivity at normal incidence for a platelet of refractive index n in air at the resonant wavelength is  $R = \left(\frac{1-n^2}{1+n^2}\right)^{-1}$  [see for example Born and Wolf (24). Since sapphire has an index of refraction of 1.76, a single platelet will have a reflectivity of 25%. In this work a two plate resonant reflector was used. It has a reflectivity of 67%. The separation and thickness of the platelets are such that the spacing between the resonant wavelengths is about 0.10 nm. Since the fluorescence linewidth of Nd in glass is about 60 nm there are many resonant wavelengths within the linewidth for which the reflectivity is high and laser oscillation is possible. When the resonant reflector was used with the Q-spoiled laser no noticeable deterioration in its optical quality was observed even after hundreds of flashes.

## (3-3) The Frequency Doubling Apparatus

After the highly intense light pulse is generated by the laser, it traverses a low pass filter to eliminate stray pump light, particularly that light in the vicinity of half the laser wavelength. In this work, a red glass plate was used. It has a transmission of 33% at  $\lambda = 1.06 \mu m$ and less than  $10^{-5}$  at  $\lambda = 0.53 \mu m$ .

Next the laser light is incident on the crystal whose nonlinear properties are to be studied. To effect velocity matching, it is necessary to adjust the orientation of the crystal with respect to the laser beam. A photograph of the mechanism of a two circle goniometer constructed for this purpose is shown in Figure 5. It was designed so that the movement for each circle of rotation is through a full 360 degrees. However, for one circle of rotation, as can be seen in the photograph. not all angles are useful due to obstructions in the light path. With the aid of a dial and vernier angles on this circle of rotation could be set and read to within 26 minutes of arc. The other circle of rotation at 90° to the first is driven by a system of worms and antibacklash gears. The gear ratio was chosen to be 1:360 so that a full revolution of the input shaft rotates the crystal by one degree. The backlash in the gear train is approximately 3 minutes of arc. For reasons explained in the next chapter, the goniometer was designed so that the nonlinear crystal could be immersed in oil. This was accomplished by mounting the goniometer in a metal container which acted both as a light shield and as an oil reservoir. Quartz windows allowed the entry and exit of the light beam.

Figure 5

# Photograph of Goniometer Mechanism



After the beam has passed through the nonlinear crystal it will contain a small amount of second harmonic and the very intense laser light. As was outlined in the introduction, there are two methods for effecting the separation. Although a medium Hilger quartz spectrograph was used initially, a system of filters has the advantage that it is much easier to align the optical components. Furthermore a greater sensitivity was obtained. A 5 cm length of saturated copper sulphate solution attenuates the laser light by about 18 orders of magnitude but yet has a 20% transmission at the doubled frequency. This filter is followed by two Baird Atomic interference filters. Each has a transmission of 50% at 0.53µm and a bandwidth (full width at half maximum) of 10 nm. The second harmonic was detected by a 1P-21 photomultiplier. To keep the transient response within acceptable limits and yield adequate gain a 1000 ohm load was used. The output signal was fed by coaxial cable to the lower beam of a dual beam Tektronix 555 oscilloscope.

In initial experiments, the signal displayed on the upper beam was proportional to the laser power. This was achieved by inserting a beam splitter in front of the low pass filter to reflect some of the laser light to a 925 phototube. Unfortunately, there is not a oneto-one correspondence between laser output and second harmonic output (36,37). The fluctuations have been attributed by Ducuing and Bloembergen (38) to the multimode nature and the less than 100% spatial coherence of solid state lasers. They showed that a more meaningful monitor could be obtained by comparing against the second harmonic intensity generated in a standard crystal. Under these conditions, changes in the spatial coherence of the laser beam from one
pulse to the next will cause corresponding variations in the two second harmonic signals, and their ratio will be constant provided the geometry of the experimental arrangement is equivalent for both the monitor and the "unknown" nonlinear crystal. The adoption of this scheme required the construction of a second goniometer and another identical system of filters and detector for monitoring the second harmonic in a standard crystal. In most experiments, it was the output from this monitor that was displayed on the upper beam of the oscilloscope. The other signal, however, was still available when required.

Figure 6 is a schematic diagram of the whole frequency doubling apparatus. As shown, a Glan prism could be mounted after the low pass filter to polarize the laser beam and another in front of the copper sulphate filter analyzed the polarization of the second harmonic. Since the apparatus was designed for use with a ruby laser as well as a Nd laser, it was necessary to avoid Nicol prisms which fail to operate at  $\sim 0.35\mu$ m because of the Canada balsam cement. In any case, Nicol prisms are more easily damaged at high power than Glan prisms since the latter use only an air gap between the calcite sections.

Also shown in Figure 6 is a phototube monitoring the laser for the purpose of providing a signal to trigger the oscilloscope. This is necessary since the interval between flashtube triggering and the evolution of the laser pulse may vary from flash to flash by as much as 20 microseconds due to small variations in rotor speed. Another complication arises because of interference when the 20 kilovolt initiating pulse is applied to the flashtube. The stray pick-up of this surge was sufficient to immediately trigger the oscilloscope long before the time

# Schematic Diagram of Frequency Doubling Apparatus

The symbols in the diagram have the following meanings:

1.Pr		LOW Pass filter		
С	=	CuSO <sub>4</sub> Filter		
IF	=	Interference Filter		
C	E	Glan Prism		
PM	1	Photomultiplier		
VA LB	11	Vertical Amplifier Lower Beam		
VA UB	=	Vertical Amplifier Upper Beam		
RF	37	Resonant Reflector		



of interest. Since shielding posed a difficult problem another solution was sought using the features of the oscilloscope. The mode "time base B triggerable once for each A delayed trigger" is ideal for this purpose. When the switch on the rotor-flashtube synchronization unit is closed, the power supply triggers the flashtube and at the same time provides a synchronization pulse to start time base A of the oscil-After a fixed delay, usually adjusted to 200µs, time base B loscope. is made "ready" i.e. triggerable. Since by this time the interference from the flashtube initiating pulse has passed, it poses no problem, and the actual oscilloscope sweep of both the upper and lower beam (time base B) is triggered by a pulse from the phototube. The signals displayed on the oscilloscope face were recorded photographically with a Dumont polaroid oscilloscope camera using ASA 10,000 polaroid film.

## (3-4) <u>Sample Preparation</u>

In this work, samples of potassium dihydrogen phosphate  $(KH_2PO_4)$ , ammonium dihydrogen phosphate  $(NH_4H_2PO_4)$ , calcite  $(CaCO_3)$ , and nickel sulphate hexahydrate  $(NiSO_4.6 H_2O)$  were used as nonlinear crystals. Initial experiments were carried out with crystals of KDP, ADP, and NiSO\_4.6 H\_2O grown from water solutions. Later experiments used higher quality KDP and ADP crystals grown at McMaster University and a large NiSO\_4. 6 H\_2O crystal purchased from Semi-Elements Inc. The calcite crystals were made available through the Physics Department at McMaster University.

In most experiments, it was necessary to cut the crystals into the form of platelets with surface normals approximately in the phase matching direction. Fortunately, all the crystals used are uniaxial. Hence the direction of the optic axis can be determined from symmetry. The KDP and ADP crystals are tetragonal, belonging to the point group 42m while NiSO<sub>4</sub>.6 H<sub>2</sub>O, also tetragonal, belongs to the point group 422. For these crystals the direction of the optic axis is in the direction of the four-fold axis. On the other hand, the calcite crystals are trigonal, belonging to the point group  $\overline{3}m$  and the optic axis is in the direction of the three-fold axis. The orientation of the other crystallographic directions were determined from the crystal habit as found in Winchell's book (39).

The platelet was formed by first cutting a surface on the crystal which made an angle of  $(90-\theta_m)$  degrees with the optic axis, where  $\theta_m$  is the angle between a phase matching direction and the optic axis. This surface was ground with successively finer grades of grinding powder and then polished to obtain a "window glass" finish. The normal to the surface was usually within two degrees of a phase matching direction. A second surface was cut parallel to the first. By a similar process of grinding and polishing the required platelet was completed.

## (3-5) Procedure

In frequency doubling experiments, the initial step was to set up the Q-spoiled laser to operate in a single pulse mode with a reproducible pulse height. The various components of the frequency doubling apparatus were then aligned along the path of the laser beam. This was achieved by inserting a piece of black paper into the laser beam and

locating the exact position of the light path by the burn spot left on the paper. With no nonlinear crystal in the goniometer, the frequency doubling apparatus was made light tight. This was confirmed by the presence of no output signal from the second harmonic detector when the Q-spoiled laser was operated. With the nonlinear crystal mounted in the goniometer, the crystal orientation was varied until an output signal was observed. Since the signal occurred in time coincidence with the laser pulse, it was either doubled frequency or laser light. The latter choice was eliminated by removing the crystal and observing the disappearance of the signal. Hence, the presence of the nonlinear crystal was required to produce the signal. There was the remote possibility that with the crystal in position, light from the laser was being scattered into the second harmonic detector. This possibility was also eliminated by replacing the nonlinear crystal with a "linear" sample and observing no signal output for any orientation of the sample.

After this preliminary procedure, the apparatus was ready for use. Usually the first experiment performed, was to measure the amount of doubled frequency as the crystal was rotated through phase matching. In a typical experiment, the pulse heights of the monitor and the second harmonic signal were recorded for 6 to 12 flashes at each angular position. For a monitor signal directly proportional to the laser power, the ratio of the second harmonic signal to the square of the monitor signal was determined. The average value of this ratio and its r.m.s. deviation were computed from the measurements taken at each crystal orientation. These ratios were plotted on a graph as a function of the crystal angular position to form a phase matching curve. The r.m.s.

deviation at the peak of the curve varied from 30% to 40%. The actual fluctuations in the ratio could be as high as a factor of 4. When a standard nonlinear crystal was used as a monitor, a similar averaging procedure was used, except the ratio taken was the second harmonic signal to the monitor signal. With this arrangement, the r.m.s. deviations decreased to 10%. This error represents the reproducibility of the results and not the true error. There may be systematic effects depending on laser beam divergence, lack of 100% coherence, and the surface and optical quality of the nonlinear crystal.

The details of the other experiments will be given, together with their results in the next chapter.

#### CHAPTER IV

#### EXPERIMENTAL RESULTS

## (4-1) Operating Characteristics of the Q-spoiled Laser

When a Nd<sup>3+</sup>:CaWO<sub>4</sub> Q-spoiled laser was first operated, it was immediately observed that the laser output consisted of several pulses instead of a single pulse as was expected. The pulses were 30 to 100 ns wide with a separation of 0.1 to 0.3 µs. Since a high power output is required for frequency doubling experiments, it was not desirable to have the Q-spoiled laser operate in this multipulse fashion with the output energy divided among several individual pulses. An investigation of the multipulse phenomena was therefore undertaken.

From the beginning, it was realized that these multipulses did not have their origin in the relaxation oscillations that are found in an ordinary laser output. Near threshold in this crystal, the spikes in the relaxation oscillations were 0.5 $\mu$ s wide and regularly spaced at intervals from 10 to 20 $\mu$ s. It was also found that the output characteristics of the rotating prism Q-spoiler depended on many parameters. In particular, two of the more interesting ones are the rotational speed of the prism and the energy of excitation applied to the flashtube. The following qualitative results were found for Nd<sup>3+</sup>:CaWO<sub>4</sub> Q-spoiled laser. They are typical of rotating Q-spoiled lasers (40) but, of course, the particular numbers vary with the quality and the size of the crystal, the efficiency of the flashtube-to-crystal coupling, etc.

Figure 7 shows oscilloscope traces of the Q-spoiled laser output at a constant excitation energy and different rotational speeds. The number of multipulses is seen to decrease with increasing rotor speed until single pulse operation is reached. This change is accompanied by a decreased multipulse spacing and a pulse width narrowing. With still greater rotor speed, the height of the single pulse grows. The peak power changes by a factor of 6 while the pulse width decreases from 100 ns to 30 ns for the range of rotors speeds covered in the figure. The complementary experiment, rotor speed constant while the excitation is varied, was also carried out. The results are shown in Figure 8. At low excitation the laser output consists of a single pulse. Increasing the excitation produces additional pulses. The peak power actually decreases with increasing excitation for the case shown in Figure 8.

In addition to the rotor speed and flashtube excitation parameters just described, the Q-spoiled laser output also varied with the rotor-flashtube synchronization, the vertical position of the prism roof edge, the reflectivity of the output reflector, and the cavity length. After the publication of results on Q-spoiling with a rotating prism (40,41) while this work was in progress, the investigation was not pursued to its conclusion.

Since most of the frequency doubling experiments were carried out using a Q-spoiled Nd-glass laser, a summary of its operating and output characteristics will be given. A noticeable difference between the Nd-glass Q-spoiled laser and the Nd<sup>3+</sup>:CaWO<sub>4</sub> was the lower rotational speeds at which single pulse operation was possible. Furthermore, because of its larger size a greater energy output was also available.

# Laser Output v.s. Time for Different Rotor Speeds

The figure consists of a series of oscilloscope traces of the laser output for different rotational speeds (the numbers are revolutions/second). In each case the flashtube input energy was kept constant at 190 joules.



## Laser Output v.s. Time for Different Excitation Energies

The figure consists of a series of oscilloscope traces showing the laser output for different flashtube excitation energies (in joules). In each case the prism rotational rate was kept constant at 830 rps.



Using a TR6 energy meter (Control Data Corp.) an energy of 0.3 joules was measured in single pulse operation. Since the pulse width at half maximum was about 30 ns and the spot size was 0.5 cm<sup>2</sup>, a peak power of 20 megawatts/cm<sup>2</sup> was obtained. This is to be compared with the 1 megawatt/cm<sup>2</sup> obtained from the doped  $CaWO_{L}$ .

For the experiments in frequency doubling it is necessary to know the polarization and the divergence of the laser beam. Although an unpolarized output was expected from Nd-glass, it is not quite so obvious that the prism in the cavity cannot have an effect. Experimentally the laser light emitted from the Nd-glass Q-spoiler was found to be unpolarized. However, after extensive use, this ceased to be the case and the laser beam became 90% polarized parallel to the roof edge indicating that the laser cavity favoured oscillation in this plane. It was observed that the glass near the roof edge of the prism had become damaged. Since rotation of neither the laser crystal nor the resonant reflector caused any change in the plane of polarization it is apparent that the prism was the determining factor. It was possible to insert a glass plate into the laser cavity at an appropriate angle so that the losses for light polarized parallel to the roof edge were increased relative to the losses for light polarized perpendicular to the roof edge. When this was done an unpolarized output was again obtained.

The divergence of the laser was measured by observing the far field pattern using a 1000 mm lens. The full width at half maximum gave a value of somewhat less than 1/4 degree (.0030 ± .0007 radians) for the divergence.

### (4-2) Frequency Doubling in KDP and ADP

Using a ruby laser, frequency doubling was first observed in KDP by Giordmaine (2) and Maker <u>et al.</u> (3) and in ADP by Savage and Miller (42). Also frequency doubling using a Nd<sup>3+</sup>:CaWO<sub>4</sub> laser was observed in both these crystals by Miller and Savage (36). At that wavelength, the measured values for the phase matching angles are reported to be  $40.3^{\circ} \pm 1.0^{\circ}$  and  $41.9^{\circ} \pm 1.0^{\circ}$  in KDP and ADP respectively.

For the purpose of testing the frequency doubling apparatus, that was constructed, frequency doubling from the infrared ( $\lambda = 1.06\mu$ m) to the green ( $\lambda = 0.53\mu$ m) was observed in both KDP and ADP. The crystal platelets for the experiment were cut as described in section (3-4). A typical phase matching curve for KDP using a Nd<sup>3+</sup>:CaWO<sub>4</sub> laser is shown in Figure 9. The ordinate, in arbitrary units, is the intensity of the second harmonic divided by the square of the intensity of the laser, while the abscissa is the angle 0 in degrees with respect to an arbitrary reference. It was confirmed that it is only the O-ray component of the fundamental that is involved in the doubling process and that the second harmonic is an E-ray.

Since the induced polarization in KDP is:

$$P_{\mathbf{x}}(2\omega) = 2 P_{\mathbf{x}} \chi_{123}^{\text{EE}} E_{\mathbf{y}}(\omega) E_{\mathbf{z}}(\omega)$$

$$P_{\mathbf{y}}(2\omega) = 2 P_{\mathbf{x}} \chi_{213}^{\text{EE}} E_{\mathbf{x}}(\omega) E_{\mathbf{z}}(\omega)$$

$$P_{\mathbf{z}}(2\omega) = 2 P_{\mathbf{x}} \chi_{312}^{\text{EE}} E_{\mathbf{x}}(\omega) E_{\mathbf{y}}(\omega),$$

and the  $E_z(\omega)$  component of an O-ray is zero, only  $P_z(2\omega)$ , and hence the  $P\chi_{312}^{\Sigma E}$  coefficient of the nonlinear susceptibility, contributes to the

# Phase Matching Curve in KDP

The angle  $\theta_{i}$  between the optic axis and the laser beam direction, is measured with respect to an arbitrary reference.



production of doubled frequency light. Thus the induced nonlinear polarization should be a maximum when  $E_x(\omega) = E_y(\omega)$ , i.e. at an azimuthal angle  $\oint = 45^\circ$ . This has been observed by Maker <u>et al</u>. (3) and it was also confirmed in this study.

## (4-3) Frequency Doubling in Nickel Sulphate Hexahydrate

From the beginning, it was realized that frequency doubling in crystals belonging to the point group 422 presented an unusual situation. The symmetry restrictions on the components of the third order tensor  ${}^{P}\chi^{EE}_{ijk}$  are such that only one coefficient is nonzero. The induced polarizations are:

$$P_{x}(2\omega) = 2 P_{\chi_{123}} E_{y}(\omega) E_{z}(\omega)$$

$$P_{y}(2\omega) = 2 P_{\chi_{123}} E_{x}(\omega) E_{z}(\omega)$$

$$P_{z}(2\omega) = 0.$$

To phase match in a uniaxial negative crystal, like NiSO<sub>4</sub>.6 H<sub>2</sub>O, the fundamental frequency must be polarized as an O-ray and the second harmonic an E-ray. Since  $E_z(\omega) = 0$  for an O-ray, there can be no induced polarization at the second harmonic frequency. Of course, there could still be a non-phased matched contribution from the electric dipole term. In addition, the above consideration does not apply to higher order nonlinear effects.

Since the material absorbs strongly in the red it is impossible to use a ruby laser in a search for frequency doubling in NiSO<sub>4</sub>.6 H<sub>2</sub>O. There is, however, a transmission band in the green and one in the infrared so that a neodymium laser is ideally suited for the purpose. It was first necessary to determine whether it is actually possible to phase match at 1.06 and 0.53 $\mu$ m in NiSO<sub>4</sub>.6 H<sub>2</sub>O. This would follow from equation (2-13) if the indices of refraction n<sub>1</sub>°, n<sub>2</sub>°, and n<sub>2</sub><sup>e</sup> were known. The only data to be found in the literature are those measured by Töpse and Christiansen in 1874 (43). The values reported are given below:

Navelength in µm	Indices of	Refraction
λ	n <sup>o</sup>	n <sup>e</sup>
<b>.</b> 656	1.5078	1.4844
•589	1.5109	1.4873
.486	1.5173	1.4930
• 439	1.5228	-

By interpolation, the required values at  $\lambda = 0.53\mu m$  are  $n_2^{\circ} = 1.5140 \pm .0004$  and  $n_2^{\circ} = 1.4902 \pm .0004$ . Extrapolating into the infrared, the index of refraction for the O-ray at  $\lambda = 1.06\mu m$  was estimated to be  $n_1^{\circ} = 1.50$ . This suggested that phase matching would occur, the direction being 50° to the optic axis. Accordingly, a crystal platelet of NiSO<sub>4</sub>.6 H<sub>2</sub>O was cut and polished, following the techniques described in section (3-4), with a surface normal to that direction. The experiment was initially performed using a focused laser beam, but, subsequently, the lenses were removed since there was adequate signal using the "parallel" beam of the laser directly. A typical phase matching curve is shown in Figure 10. The large fluctuations at the peak were the result of the lack of one-to-one correspondence between the second harmonic and laser outputs.

# Phase Matching Curve in NiSO4.6 H2O

The relative second harmonic is the ratio in arbitrary units of the doubled frequency detector signal output to the square of the laser monitor signal output. The angle  $\theta$ , between the optic axis and the laser beam direction, is measured with respect to an arbitrary reference.



The polarization of that component of fundamental frequency which is the doubled frequency source was determined. This was accomplished by inserting a Glan prism into an unpolarized laser beam, and measuring the second harmonic output as the plane of polarization of the beam is varied. The result of plotting the magnitude of the relative second harmonic against the angle  $\mathcal{W}$ , measured between the plane of polarization of the laser beam and a principal plane in the crystal, is shown in part (a) of Figure 11. If only the O-ray component of the fundamental is effective, the second harmonic should be proportional to  $\sin^4 \mathcal{V}$ , while an E-ray component would be indicated by a  $\cos^4 \mathcal{V}$  dependence. The solid line is proportional to  $\sin^4 \mathcal{V}$ . Although the data appear to vary faster than  $\sin^4 \mathcal{V}$ , it is clear that an O-ray is responsible for the doubling. The discrepancy between theory and experiment probably arises due to a slight misalignment of the Glan prism.

The polarization of the second harmonic was determined in an analogous fashion by inserting a Glan prism into the doubled frequency beam. The results are plotted in part (b) of Figure 11. The solid line shows  $\cos^2 \not/$  dependence to be expected of an E-ray. Thus the above experiments in NiSO<sub>4</sub>.6 H<sub>2</sub>O indicate that O-ray at the fundamental frequency generates an E-ray at the second harmonic frequency.

## (4-4) The Phase Matching Angle in Nickel Sulphate Hexahydrate

The phase matching angle in  $NiSO_4.6 H_2O$  was measured. This was accomplished by measuring the angular diameter of the phase matching cone. For this purpose, a crystal of  $NiSO_4.6 H_2O$  was cut in the shape of a right parallelepiped. By using the fact that the optic

## Dependence of S.H. Intensity on Orientation of Glan Prism in (a)

## the Laser Beam and (b) the S.H. Beam

The second harmonic intensity was measured as the plane of polarization of (a) the laser beam and (b) the second harmonic beam was varied with a Glan prism. In both (a) and (b)  $\mathscr{V}$  is the angle between a principal plane in the crystal and the polarizing direction of the Glan prism. The solid curve in (a) is  $\sin^4 \mathscr{V}$  indicating an O-ray fundamental frequency while in (b) it is  $\cos^2 \mathscr{V}$  indicating an E-ray second harmonic.



axis is normal to the (OOI) cleavage plane, it was possible to cut the crystal with the optic axis parallel to the base of the parallelepiped. A cross-section parallel to this base is shown in Figure 12. A provisional value of 54 degrees for the phase matching angle, determined in an earlier experiment, was assumed in the construction of the parallelepiped. The crystal was then mounted in the goniometer so that it could be rotated about an axis perpendicular to the optic axis. As indicated in Figure 12, there are two directions through the crystal for which phase matching can be obtained and the angle between them is  $2\theta_m$ . Hence, from an experimental measurement of the change in crystal orientation between these two directions, the phase matching angle can be determined.

Because the phase matching directions are not necessarily normal to the surfaces of the parallepiped, there is a slight complication. The second harmonic detector has a relatively wide aperture and thus refraction of the beam on leaving the crystal is of no concern. However, there will be an error due to refraction of the laser beam at the front surface of the crystal. This can be minimized by immersing the crystal in an index matching liquid. From Figure 12 it can be seen that the measured angle is given by  $\mathcal{V}_{exp} = 2\theta_m + (\beta'-\beta) + (\alpha'-\alpha)$  where  $\alpha$ ,  $\beta$ ,  $\alpha'$ , and  $\beta'$  are indicated in the figure. Since Snell's law is valid in a birefringent medium if the wave normal directions are considered and since  $\alpha$ ,  $\alpha'$ ,  $\beta$  and  $\beta'$  are small it follows that

$$\mathcal{Y}_{exp} = 2\theta_m - \left(1 - \frac{n_1^o}{n}\right) (\alpha + \beta)$$

### The Measurement of the Phase Matching Angle

A schematic diagram showing the principle by means of which  $\theta_m$  was measured. The directions shown in the crystal are those of the wave normal, not the rays. If the angles  $\alpha$ ,  $\beta$ ,  $\alpha'$ , and  $\beta'$  were zero  $\theta_m = \frac{1}{2} \frac{\gamma}{\exp}$ . The corrections to allow for refraction are explained in the text. The inset at the top shows the actual experimental arrangement in which the crystal is rotated while the incident laser beam remains fixed in the laboratory.



where  $n_1^{\circ}$  and n are the refractive indices at  $\lambda = 1.06\mu m$  for the O-ray and the liquid respectively. In this work, benzyl alcohol  $(C_{6H_5}CH_2OH)$  was used for the immersion bath in the goniometer. It is transparent both in the green and the infrared, and has indices of refraction n = 1.517 and 1.576 at  $\lambda = 1.06\mu m$  and 0.53 $\mu m$  respectively. Only the former is of importance here. Since  $\alpha$  and  $\beta$  are less than 5 degrees and  $\left(1 - \frac{1.5}{1.517}\right) \sim 0.01$ , the error due to an imperfectly cut crystal was negligible. From the experimentally measured angle,  $V_{exp} = 113^{\circ} \pm 2^{\circ}$ , a phase matching angle of  $\theta_m = 56.6^{\circ} \pm 1.0^{\circ}$  was determined. The uncertainty arises because of the finite width of the phase matching curve.

As pointed out above, only a rough value of the index of refraction of the O-ray at  $\lambda = 1.06 \mu m$  could be obtained from previous It is now possible to calculate a precise value. data.  $n_1^{\circ} = 1.497 \pm 0.001$ , based on equation (2-13) and the measured phase matching angle. It should be noted, that n e cannot be determined in this way. Based on extrapolation of Topse and Christiansen's values, the best estimate is  $n_1^{e} \approx 1.47$ . This is indicated in Figure 13 where the indices of refraction of  $NiSO_4.6 H_2O$  for the laser and the doubled frequency are plotted as a function of the angle  $\theta$  between the wave normal and the optic axis. If  $n_1^{e}$  were greater than 1.483 it should be possible to obtain OE-E type phase matching. A search for frequency doubling with OE-E phase matching was carried out in one degree intervals. No augmented frequency doubling other than that at  $\theta = 56.5^{\circ}$ was observed indicating that  $n_1^e$  is very probably less than 1.483.

# Refractive Index of NiSO<sub>4</sub>.6 $H_2O$ as a function of $\theta$

The angle  $\theta$  is measured from the optic axis to the wave normal direction. Since the refractive indices of an O-ray,  $n_1^{\circ}$  and  $n_2^{\circ}$ , are independent of  $\theta$ , they are represented by straight lines in this graph. The refractive index of the E-ray,  $n_2^{e}(\theta)$ , is the solid curve from  $n_2^{\circ}$  to  $n_2^{e}$ . Phase matching occurs at the intersection of this curve with the straight line  $n_1^{\circ}$ , i.e. at  $\theta_m = 56.5^{\circ}$ . Since  $n_1^{e}$  is not known, the refractive index  $n_1^{e}(\theta)$  is drawn in the diagram as a dashed curve.



# (4-5) Azimuthal Dependence of Frequency Doubling in NiSO4.6 H2O

#### and Calcite

As mentioned in section (2-5), it is useful to determine the azimuthal dependence of the frequency doubling. What is required is a measure of the amount of second harmonic produced as the crystal orientation is altered so that the azimuthal angle  $\phi$  for the direction of light propagation changes. Of course, it is vital that the experiment be performed in such a way that any variation in the second harmonic output can be attributed to a variation in  $\phi$  and not heta.Therefore, great care is necessary to ensure that the crystal is rotated about its optic axis. This was accomplished by cutting a platelet so that the normal to the surface of the crystal was in the direction of the optic axis. The platelet was then mounted on the goniometer so that the optic axis was aligned along one of the axes of rotation. The other axis of rotation was used to adjust the orientation of the crystal for phase matching. With this geometry phase matching will occur when the laser light is obliquely incident on the crystal platelet. However, since the crystal is rotated about the optic axis, the angle of incidence and 6 will remain the same. Also, the effective thickness of the crystal will be constant. Fortunately in the case of  $NiSO_4.6$  H<sub>2</sub>O, the crystals cleave in a plane perpendicular to the optic axis so that the required platelets were easily formed. A platelet of suitable thickness was mounted on the goniometer and aligned with the aid of an autocollimator. By observing the image of the cross-hairs reflected by the crystal platelet it was possible to

obtain the necessary coincidence of the axis of rotation and the optic axis to within a few minutes of arc. There is however, one further problem. Since the index of refraction of NiSO4.6 H2O is 1.497 for the O-ray at  $\lambda = 1.06 \mu m$  the critical angle is 42°. Hence there is no angle of incidence in air which will allow the laser light to pass through the crystal at the phase matching angle of 56.5°. The difficulty was overcome by immersing the crystal in benzyl alcohol. This also essentially eliminated reflection at the surfaces. The residual loss is a constant since the angles of incidence with the front and back surfaces are independent of  $\phi$  . The results obtained for the azimuthal dependence of the frequency doubling are shown in Figure 14. Measurements were first taken at 20° intervals from  $\phi$  = -45° up to  $\phi = 135^{\circ}$ . Intermediate points were obtained by rotating backwards from  $\phi = 125^{\circ}$  to  $\phi = -35^{\circ}$ . At each angle, phase matching was checked, and the average over 12 flashes was determined. Within the errors, the results are independent of  $\mathscr{O}$ . In order to assess the possibility of a weak angular variation the data were Fourier analysed. The results are

 $S(\phi) = (1.032 \pm 0.012) + (0.003 \pm 0.018) \cos 2\phi - (0.011 \pm 0.016) \sin 2\phi$ - (0.011 \pm 0.017) \cos 4\phi + (0.001 \pm 0.017) \sin 4\phi - (0.010 \pm 0.018) \cos 6\phi - (0.002 \pm 0.017) \sin 6\phi - (0.012 \pm 0.017) \cos 8\phi + (0.003 \pm 0.017) \sin 8\phi.

Except for the constant term which is the solid line drawn on the graph in Figure 14, the other amplitudes are all consistent with being zero.

The Azimuthal Dependence of the Frequency Doubling in  $NiSO_{4} \cdot 6 + 0.2$ 

The angle  $\phi$  is measured between the x-crystallographic axis and a principal plane containing the laser beam. The solid line drawn on the graph is the constant term in a Fourier analysis of the data.



A similar experiment was carried out in calcite, since the results of such an experiment have not been reported previously. Unlike NiSO4.6 H<sub>2</sub>O calcite does not cleave in a plane perpendicular to its optic axis. It was therefore necessary to grind and polish a platelet with the 3 fold axis normal to its surface. To confirm that the grinding had been properly carried out the resulting platelet was observed under a polarizing microscope. The optic axis was found to differ from the platelet normal by one degree but this was considered to be adequate alignment for the experiment. As mentioned previously frequency doubling in calcite has been observed by Terhune (6) and is of the OO-E type. Since the critical angle for the O-ray in calcite is 37.5° at  $\lambda = 1.06 \mu m$  and the phase matching angle is 18.1°. the azimuthal dependence for calcite was measured with the crystal in air. This necessitated using an angle of incidence of 30.7° with an accompanying 9% reflection loss in the laser intensity. Since the birefringence of calcite is large, the full width at half maximum of the phase matching curve was only 12 minutes of arc. Hence great care had to be taken during the measurements to ensure that phase matching was maintained. This necessitated re-measuring the portion of the phase matching curve near its peak at each angle p. The measurements were taken in alternate order as for NiSO4.6 H2O, but in this case the entire range,  $0 \le \phi \le 360^\circ$ , was scanned. The resulting azimuthal dependence is shown in Figure 15. Although the data are somewhat erratic a  $\sin 3\phi$  dependence is clearly visible. In a Fourier analysis of the data. the only statistically significant terms are

# Azimuthal Dependence of Frequency Doubling in Calcite

The angle  $\phi$  is measured between the x-crystallographic axis and a principal plane containing the laser beam. The solid curve is  $S(\phi) = 0.71 \div 0.24 \sin 3\phi$ . It was obtained from a Fourier analysis of the data.


$$S(\phi) = (0.71 \pm 0.01) + (0.24 \pm 0.01) \sin 3\phi$$
.

Pershan (26) has predicted that the azimuthal dependence should be of the form

 $(A*B \sin 3\phi)^2 = (A^2+\frac{1}{2}B^2) + 2AB \sin 3\phi - \frac{1}{2}B^2 \cos 6\phi$ where for a lossless nonmagnetic material A and B are real constants. By fitting the first two terms in this expression to  $S(\phi)$ , the values  $A = 0.843 \pm 0.004$  and  $B = 0.14 \pm 0.01$  were determined. Hence the ratio of the constant term to the amplitude of the  $\sin 3\phi$  term is  $\frac{A}{B} = 6.0\pm0.4$ . Although the  $\cos 6\phi$  term was not observed, its absence is understandable, since the above values of A and B predict a value of only 0.01 for the coefficient of the  $\cos 6\phi$  term, which would be lost in the experimental error. An estimate of the minimum detectable amplitude for the  $\cos 6\phi$  term is about 0.05. Hence the experimental data **are** consistent with real values for A and B, but does not exclude the possibility of a phase difference as large as  $60^\circ$  between complex values for A and B.

# (4-6) Frequency Doubling Dependence on Path Length In NiSO4.6 H2O

Since nickel sulphate hexahydrate absorbs somewhat at both the laser and second harmonic frequencies, it is interesting to observe how the intensity of the second harmonic varies with crystal thickness. Platelets of various thickness were formed by cleaving sections perpendicular to the optic axis. The smallest thickness that could be obtained was 0.020 cm. Each crystal in succession, was mounted on the goniometer and immersed in benzyl alcohol. The relative intensities of doubled frequency at the peak of the phase matching curve are recorded in Table I. The effective path length traversed by the beam in the

		· · · · · · · · · · · · · · · · · · ·
Platelet	Effective	Relative
Thickness	Path Length	Second
d (cm)	L ( cm)	Harmonic
1.31	2•37	5.8 <b>*</b> 3.0
1.08	1.96	17 ± 3
0.985	1.79	32 ± 6
0.838	1.52	74 ± 9
0.571	1.17	109 <b>±</b> 12
0.338	0.612	490 ± 45
0.165	0.299	870 ± 70
0.107	0.193	1080 ± 70
0.063	0.11.5	1160 ± 70
0.043	0.078	1080 ± 60
0.030	0.055	800 ± 20
0.024	0.044	640 ± 15
0.020	0.037	675 ± 35
· · · · · · · · · · · · · · · · · · ·		· · · · ·

Table I

Frequency Doubling Dependence on Path Length in NiSO ...6H20

crystal is given by  $\ell$  = d sec  $\theta_m$  where  $\theta_m$  = 56.5° and d is the thickness of the cleaved platelet. The data of Table I are plotted on a logarithmic scale in Figure 16.

In section (2-3) a theory of second harmonic generation in absorbing crystals was presented. For a nearly parallel beam, the intensity of the second harmonic should have the form

$$S(2\omega) = A e^{-\gamma l} \frac{\sinh^2 \xi l}{\xi^2}$$
(2-11a)

where  $\ell$  is the effective crystal thickness and  $\gamma$  and  $\xi$  are given by

$$Y = 2\alpha_1 + \alpha_2$$
  $\dot{\xi} = \left| \alpha_1 - \frac{1}{2}\alpha_2 \right|$ . (2-11b)

The amplitude absorption coefficients of the O-ray at  $\gamma = 1.06\mu m$ and the E-ray at  $\gamma = 0.53\mu m$  are denoted by  $\alpha_1$  and  $\alpha_2$  respectively. Using a spectrophotometer, it was found that  $\alpha_1 = 13.5 \pm 0.5 \text{ cm}^{-1}$ . Since NiSO<sub>4</sub>.6 H<sub>2</sub>O is a uniaxial crystal, the absorption coefficient of the E-ray is anisotropic. In the phase matching direction, it was found that  $\alpha_2 = 1.15 \pm .05 \text{ cm}^{-1}$ . Therefore, from (2-11b),  $\gamma = 28.2 \pm 1.0 \text{ cm}^{-1}$  and  $\xi = 12.9 \pm 0.5 \text{ cm}^{-1}$ . With these values and the aid of equation (2-12), the optimum thickness for maximum doubled frequency output was calculated to be  $0.12 \pm 0.05$  cm. In Figure 16, it can be seen that the data peak at essentially this value. The solid curve is a plot of expression (2-11a) with the valuea for  $\gamma$  and  $\xi$ given above. The curve, which was normalized to fit at the maximum is in good agreement with the data.

## Figure 16

Frequency Doubling Dependence on Path Length in NiSO<sub>4</sub>.6 H<sub>2</sub>O The solid curve,  $S(2\omega) = \frac{A}{\xi} e^{-\gamma \ell} \sinh \xi \ell$ , is the theoretical expression for the second harmonic intensity emitted from an absorbing crystal. The values of  $\gamma$  and  $\xi$  in NiSO<sub>4</sub>.6 H<sub>2</sub>O are 28.2 cm<sup>-1</sup> and 12.9 cm<sup>-1</sup> respectively, and the curve has been normalized to fit the data at the maximum.



# (4-7) <u>The Relative Magnitude of the Frequency Doubling in</u> NiSO<sub>4.6</sub> H<sub>2</sub>O, Calcite, and KDP

It is very difficult to make an absolute measurement of the magnitude of a frequency doubling coefficient since this involves absolute calibration of the detectors, a knowledge of the intensity distribution in the beam cross section and the multimode structure of the beam etc. Since these problems have been overcome by Ashkin <u>et al</u>. (12) using a gas laser, an absolute measure of the amplitude for frequency doubling in NiSO<sub>4</sub>.6 H<sub>2</sub>O can be obtained by a direct comparison of this material with others. There are still some uncertainties due to beam divergence, crystal inhomogeneity, and lack of 100% coherence, but the difficulties are much fewer.

In order to compare the magnitude of the frequency doubling in  $NiSO_4.6 H_2O$  with that in calcite and KDP, crystal platelets of each were cut as outlined in section (3-4) so that phase matching could be obtained at normal incidence. In the case of calcite the phase matching angle for frequency doubling using a Nd-glass laser was calculated from refractive index data (44) to be  $18.1^\circ$ . The intensity produced in each platelet at phase matching was measured relative to the signal  $S_m$  from a detector monitoring the second harmonic produced in a  $NiSO_4.6 H_2O$  crystal. The results are shown in Table II. A direct comparison of doubled frequency intensity produced in each crystal can be obtained by eliminating the monitor signal. Then

$$\frac{s_1}{s_2} = (2.7 \pm 0.7) \times 10^6$$
$$\frac{s_1}{s_3} = (4.4 \pm 1.0) \times 10^6$$

i	Material	Thickness (cm)	θ <sub>m</sub> (degrees)	ø (degrees)	Si Sm
1	KDP	0.19	40.3	45	(3.3 <u>*</u> 0.8) x 10 <sup>6</sup>
2	Calcite	0.28	18.3	0	1.24 <u>+</u> 0.06
3	NiSO4.6H20	0.28	56.5	45	0.75 ± 0.03

Table II
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Relative Second Harmonic Intensity Produced in KDP, Calcite, and  ${\rm NiSO}_{\underline{l}}{\scriptstyle .}6{\rm H}_{\underline{2}}{\scriptstyle 0}$ 

and

$$\frac{s_2}{s_3} = (1.65 \pm 0.10)$$

The corrections that must be made in order to obtain the magnitudes of the nonlinear susceptibilities are discussed in the next chapter.

Since calcite has a large birefringence it is also possible to observe OE-E type phase matching at  $9 = 25.3^{\circ}$ . Using the same platelet, the intensity of the second harmonic at that angle was measured to be

$$\frac{S_4}{S_m} = 0.023 \pm 0.003$$

Hence in calcite the relative magnitude of the OO-E second harmonic generation to the OE-E nonlinearity is

$$\frac{s_2}{s_4} = 54 \pm 7$$

#### CHAPTER V

#### DISCUSSION OF RESULTS

#### (5-1) The Rotating Prism Q-spoiled Laser

The appearance of multipulsing was explained qualitatively by Benson and Mirarchi (40) and Daly and Sims (41) in terms of the rotating prism being a slow Q-switch. Whether a particular Q-spoiling device is slow or fast depends on the relative values of two parameters, the switching time  $t_g$  and the photon build up time  $t_p$ . The latter, which depends on the length of the laser cavity is defined as the time it takes for the photon flux to build up from its fluorescence value to its peak value. For a typical laser,  $t_p \approx 200$  ns. On the other hand, the switching time is the time which elapses as the threshold for laser oscillation changes from a high initial value to its minimum value. An estimate of this quantity can be obtained by measuring the threshold for laser action as a function of the angular alignment of an adjustable stationary reflector. For a rotor speed of 500 rps, a typical value of  $t_g$ , for a Nd<sup>3+</sup>: CaWO<sub>4</sub> Q-spoiled laser, is ~1400 ns. Since  $t_g >> t_p$ , this is the case of slow Q-switching.

The phenomenon of the multipulsing can but be explained in terms of some diagrams. The case of slow Q-switching is shown in part (a) of Figure 17. The dashed line represents the slow change in threshold for laser oscillation from a high initial value to its mini-

### Figure 17

## The Switching Speed of a Q-spoiled Laser

Part (a) is the case of slow Q-switching, and Part (b) is that for fast Q-switching. In the upper half of the figure, the dashed lines represent the change in threshold for laser oscillation as the rotating mirror approaches alignment, whereas the solid lines represent the population inversion. In the bottom half a schematic plot of the light output from the Q-spoiled laser is drawn for each case.



mum value while the solid line shows the population inversion which has a high initial value due to optical pumping. When the population inversion exceeds the threshold value, the light pulse will begin to evolve. The evolution of the light pulse causes a rapid decrease in the number of excited atoms. When the population *inversion* falls below the threshold value, the pulse begins to diminish. Since  $t_{s} > t_{p}$ , it is possible for more than one light pulse to evolve before minimum threshold is reached. In the lower part of the diagram a schematic plot of the light output is shown.

In a similar manner, part (b) of Figure 17 illustrates the case  $t_s \sim t_p$ . The light output is now a single pulse containing virtually all the energy stored in the population inversion. In terms of the parameters,  $t_s$  and  $t_p$ , the observed dependence of the multipulses on rotational speed of the prism and flashtube excitation are understand-able qualitatively.

The rotating prism Q-switch is different from other Q-spoilers since the threshold for laser oscillation near alignment varies from a maximum value to a minimum value and then returns to a maximum value again. This is to be compared with a Kerr cell Q-switch in which the threshold is reduced and remains at a low value. Since the threshold for laser oscillation remains low only for a short time, there is an optimum switching time  $t_s \approx t_p$ , for which maximum single pulse power is obtained. For  $t_s < t_p$ , single pulse operation occurs, but the peak power is reduced since the losses are increasing before the pulse has fully evolved. Such an effect was not observed in this study, with a Nd<sup>3+</sup>:CaWO<sub>4</sub> Q-spoiled laser, but it has since been seen by Hill (45) with a Nd-glass Q-spoiled laser.

Since the switching time depends not only on the rotor speed but also on the laser beam divergence and hence on the optical quality of the laser crystal, that factor must be considered in choosing a laser crystal for Q-spoiling. In general, neodymium doped  $CaWO_4$  is of lower optical quality than Nd-glass. Hence for a given rotor speed and flashtube excitation,  $t_s$  is shorter in a Nd-glass Q-spoiled laser than in a Nd<sup>3+</sup>:CaWO<sub>4</sub> one, so that single pulse operation is much more easily obtained in the former than in the latter.

# (5-2) Frequency Doubling in NiSO<sub>4</sub>.6 H<sub>2</sub>O

In the experiments on frequency doubling in NiSO<sub>4</sub>.6 H<sub>2</sub>O, one might question whether the photomultiplier output was really due to green light generated by frequency doubling. Since the output signal disappeared when the crystal was removed, the phenomenon is definitely a characteristic of the crystal. The wavelength of the doubled frequency was not actually measured, but the interference filters used had a pass band of about 10 nm at 530 nm. If some process other than frequency doubling is involved, that process must explain the following facts. Firstly, the output signal is only observed for  $\theta = 56.5^{\circ}$  and arbitrary  $\phi$ , and as shown in Figure 10, it has a strong dependence on  $\theta$  about  $\theta = 56.5^{\circ}$ . Secondly, as indicated in Figure 11, the green light produced is polarized as an E-ray, and only the O-ray component of the laser light is useful in generating the green light.

Since the laser emits more than one frequency of light, sum frequency generation is a possibility. As described in section (2-1) the susceptibilities,  ${}^{P}\chi_{ijk}^{EE}(\omega_{1} + \omega_{2})$  for optical summing are not symmetric in j and k. Hence for a crystal with 422 symmetry, the induced polarizations at  $\omega_{1} + \omega_{2}$  are

$$P_{\mathbf{x}}(\omega_{1} + \omega_{2}) \stackrel{P}{=} \chi_{123}^{\text{EE}} E_{\mathbf{y}}(\omega_{1}) E_{\mathbf{x}}(\omega_{2}) \stackrel{P}{+} \chi_{123}^{\text{EE}} E_{\mathbf{z}}(\omega_{1}) E_{\mathbf{y}}(\omega_{2})$$

$$P_{\mathbf{y}}(\omega_{1} + \omega_{2}) = \stackrel{P}{-} \chi_{123}^{\text{EE}} E_{\mathbf{x}}(\omega_{1}) E_{\mathbf{z}}(\omega_{2}) \stackrel{P}{-} \chi_{123}^{\text{EE}} E_{\mathbf{z}}(\omega_{1}) E_{\mathbf{x}}(\omega_{2})$$

$$P_{\mathbf{z}}(\omega_{1} + \omega_{2}) = \stackrel{P}{-} \chi_{312}^{\text{EE}} \left[ E_{\mathbf{x}}(\omega_{1}) E_{\mathbf{y}}(\omega_{2}) - E_{\mathbf{y}}(\omega_{1}) E_{\mathbf{x}}(\omega_{2}) \right].$$

For two O-rays with electric fields

$$E(\omega_1) = \begin{pmatrix} \sin \phi \\ -\cos \phi \\ 0 \end{pmatrix} E_1 e^{i(\vec{k}_1 \cdot \vec{r} - \omega_1 t)} E(\omega_2) = \begin{pmatrix} \sin \phi \\ -\cos \phi \\ 0 \end{pmatrix} E_2 e^{i(\vec{k}_2 \cdot \vec{r} - \omega_2 t)}$$

at frequencies  $\omega_1$  and  $\omega_2$  respectively, the polarizations  $P_x(\omega_1 + \omega_2)$ and  $P_y(\omega_1 + \omega_2)$  are zero since both  $E_z(\omega_1)$  and  $E_z(\omega_2)$  are zero.  $P_z(\omega_1 + \omega_2)$  is also zero because for a parallel beam,

$$\mathbb{E}_{\mathbf{x}}(\omega_{1}) \mathbb{E}_{\mathbf{y}}(\omega_{2}) = \mathbb{E}_{\mathbf{y}}(\omega_{1}) \mathbb{E}_{\mathbf{x}}(\omega_{2}).$$

Hence the possibility of electric dipole optical summing can be rejected.

If the index of refraction of the O-ray at  $\lambda = 1.06\mu m$  were known, it would be possible using (2-13) to calculate the phase matching angle  $\theta_m$  and compare it with the experimentally measured value,  $\theta_m = 56.6 \pm 1.0$ degrees. Unfortunately, no data for  $n_1^0$  is available, so such confirmation is impossible. Nevertheless, it appears quite safe to conclude that frequency doubling was indeed observed. As shown in section (4-3), frequency doubling in NiSO<sub>4</sub>.6 H<sub>2</sub>O by an O-ray cannot be attributed to radiation from an induced electric dipole moment. It is not a surface effect either. Doubled frequency produced at the boundary of a crystal would not have the dependence on path length shown in Figure 16. It is logical, therefore, to attribute this doubled frequency to one or more higher order terms, as was done in the case of calcite by Terhune <u>et al</u>. (6). Evidence to support this view can be found in the measurements on the relative magnitudes of the frequency doubling in KDP, calcite, and NiSO<sub>4</sub>.6 H<sub>2</sub>O. In chapter II equations (2-15a) and (2-15b) give the second harmonic intensity,  $S(2\omega)$ , to be expected in transparent and absorbing platelets respectively. The ratio of intensities in two nonlinear materials, i and j, is therefore

$$\frac{S_{i}}{S_{j}} = \frac{R_{i}}{R_{j}} \left(\frac{n_{j}}{n_{i}}\right)^{3} \left(\frac{\ell_{i}}{\ell_{j}}\right)^{2} \left(\frac{A_{i}}{A_{j}}\right)^{2} \qquad \frac{F(\beta_{i} \ell_{j} \Delta)}{F(\beta_{j} \ell_{j} \Delta)}$$

where the subscripts i, j = 1,2,3 denote KDP, calcite, and NiSO<sub>4</sub>.6  $H_2$ O respectively, and the quantities A<sub>1</sub> are the amplitudes for frequency doubling in each case. For absorbing crystals

$$F(\beta_{i} \boldsymbol{\ell}_{i} \Delta) \equiv K = \frac{e^{-\gamma \boldsymbol{\ell}_{F}(\boldsymbol{\xi} \Delta)}}{\boldsymbol{\ell}^{2}}$$
(2-15c)

where the quantity K includes both the effects of absorption and beam divergence. The values of the constants in the above equations for the crystals used in the relative intensity measurements are listed in Table III. In the case of NiSO4.6 H20 the formula for a nearly parallel

beam

$$K = \frac{e^{-\gamma \ell} \sinh^2 \xi \ell}{\xi^2 \ell^2} \left[ 1 - \frac{(\beta \ell \Delta)^2}{4} \left( \frac{1}{\xi^2 \ell^2} - \frac{1}{\sinh^2 \xi \ell} \right) \right]$$

was used in evaluating K. The justification is that the full width at half maximum of the phase matching curve, which can be seen in Figure 10 to be 1.0  $\pm$  0.2 degrees, is greater than the beam divergence. Furthermore, as was shown in section (2-4), for  $\sinh \frac{1}{5}\ell \gg 1$  and a nearly parallel beam, the width of the phase matching curve approaches  $W = \frac{2\frac{1}{5}}{\beta}$ . For the platelet under consideration,  $\sinh \frac{1}{5}\ell = 18.3$  and  $W = 1.1 \pm .05$ degrees which is in good agreement with the observed value. Using the experimental intensity ratios from section (4-7) and the constants in Table III. the amplitude ratios are

$$\frac{A}{A_1} = (7 \pm 4) \times 10^{-4}$$

$$\frac{A_3}{A_1} = (3 \pm 1) \times 10^{-3}$$

 $\frac{A_3}{A_2} = 4.0 \pm 1.0.$ 

and

In the case of KDP (22),  $A_1 = \chi_{312}^{\text{EE}} \sin \theta_m \sin 2\phi$  where  $\theta_m = 40.3^\circ$ and  $\phi = \frac{\pi}{4}$ . Since Ashkin et al. (12) have measured  $\chi_{312}^{\text{EE}}$  to have the value (3.0 ± 1.0) x 10<sup>-9</sup> esu, the absolute values of the amplitudes for frequency doubling in calcite and NiSO<sub>4.6</sub> H<sub>2</sub>0 are

$$A_2 = (14 \pm 8) \times 10^{-13}$$
 esu  
 $A_3 = (6 \pm 3) \times 10^{-12}$  esu.

and

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Relevant Constants for Frequency Doubling Amplitude Ca	for	requency	Doubling	Amplitude	Calculations
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i	l	2	3
angen men kan gan pangan segara da pangan kan dina da pangan kan dina da pangan segara segara pangan pangan ka Internet	KDP	Calcite	NiS04. 6 H20
ni	1.495	1.6434	1.497
$R_{i} = \frac{64 n_{i}^{3}}{(n_{i}+1)^{6}}$	.883	<b>.</b> 833	.885
(cm)	.19	•28	.28
2 <b>Δ(radians</b> )	.003 ± .0007	.003 ± .0007	.003 ± .0007
β <sub>i</sub> (cm <sup>-1</sup> )	2430	6950	1290
β <sub>i</sub> ℓ <sub>i</sub> Δ	0.7 + 0.2	2.9 🕂 0.7	0.5 ± 0.1
F(β <sub>i</sub> ℓ <sub>i</sub> Δ)	•95 <b>±</b> •03	0.5 ± 0.2	K=0.014 <u>+</u> 0.002

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The value of  $A_2$  compares favourably with the value of  $10^{-12}$  estimated from the results of Terhune <u>et al</u>. (6). It can be seen that the amplitude for frequency doubling in NiSO<sub>4</sub>.6 H<sub>2</sub>O is considerably smaller than in KDP. This indicates that higher order terms are responsible.

The question of which higher order terms can produce frequency doubling when the amplitude for electric dipole frequency doubling is zero has been considered in section (2-4). There it was shown that both magnetic dipole and electric quadrupole frequency doubling is possible. The free energy for the magnetic dipole effects resulted in the induced moments

$$P_{i}(\omega) = {}^{P}\chi_{ijk}^{EH} E_{j}(\omega) E_{k}(\omega)$$

$$M_{k}(\omega) = M \chi_{mlk}^{EE} E_{m}(\omega) E_{l}(\omega)$$

where the susceptibilities  ${}^{P}\chi_{ijk}^{EH}$  and  ${}^{M}\chi_{m\ell k}^{EE}$  are pure imaginary for a lossless nonmagnetic material. On the other hand, the quadrupole effects resulted in the induced moment

$$Q_{ij}(2\omega) = Q \chi_{ijk\ell}^{EE} E_k(\omega) E_\ell(\omega)$$

where  ${}^{Q}\chi_{ijk\ell}^{EE}$  is real for a lossless nonmagnetic substance. In Table IV the nonzero coefficients for the susceptibilities  ${}^{P}\chi_{ijk}^{EE}$ ,  ${}^{P}\chi_{ijk}^{EH}$ ,  ${}^{M}\chi_{m\ell k}^{EE}$ , and  ${}^{Q}\chi_{ijk\ell}^{EE}$  are listed for a crystal with 422 symmetry.

As mentioned previously in section (2-5), a measurement of the azimuthal dependence may make it possible to distinguish among the various high order terms. Also in that section, it was shown how the azimuthal dependence for electric dipole frequency doubling can be deter-

T	ab]	-0	IV
*	an	-0	- <b>1</b>

The Frequency Doubling Susceptibilities in NiSO1.6H20

jk	11	22	33	23	32	13	31.	12	21
123	0	0	0	123	123	0	0	0	0
	0	0	0	0	0	-123	-123	0	0
	0	0	0	0	0	0	0	0	0

 ${}^{P}\chi_{ijk}^{EE}$  = (ijk)

 ${}^{\mathrm{P}}\chi^{\mathrm{HH}}_{\mathrm{ijk}}$  = (ijk)

jk	11	22	33	23	32	13	31	12	21.
1	0	0	0	123	132	0	0	0	0
2 3	- 0 - 0	0	´ 0 0	0	0	-123	-132 0	-0 312	0 -321

 $^{M}\chi_{mlk}^{EE}$  = (mlk)

1k	11	22	33	23	32	1.3	31	12	21.
1	0	0	0	0	132	0	0	0	0
2	0	0	0	0	0	0	132	0	0
3	0	0	0	0	0	0	0	132	-132

 $^{\rm Q}\chi^{\rm EE}_{\rm ijk\ell}$  = (ijkl)

K ki	77	22	32	23	30	12	27	12	- 27
	ىلىياء 	66		دے	26		<u>ــر</u>	1.4	21
11	1111	1122	1133	0	Ó	0	0	0	0
22	1122	1111	11.33	0	0	0	0	0	0
33	3311	3311	3333	0	0	0	0	0	0
23	0,0,1	0	0	1313	1313	0	0	0	· 0
32	0	0	0	1313	1313	0	0	0	0
13	0	0	0	0	0	1313	1.313	0	0
31	0	0	0	0	0	1313	1313	0	0
12	0	· 0	· 0	0	0	0	0	1212	1212
21	0	0	0	0	0	0	0	1212	1212

mined. These calculations have been extended to electric quadrupole and magnetic dipole frequency doubling in the Appendix. The azimuthal dependences for these effects with OO-E phase matching are listed in Table V. It can be seen that only two terms,  ${}^{Q}\chi^{\rm EE}_{ijk}$  and  ${}^{P}\chi^{\rm EH}_{ijk}$  are effective in NiSO<sub>4</sub>.6 H<sub>2</sub>O. Since the second harmonic intensity is proportional to  $J_{\rm eff}^{2}$ , and hence  $\oint^{2}$ , the frequency doubling intensity for a  ${}^{Q}\chi^{\rm EE}_{ijk\ell}$  term is proportional to (A + B cos 4 $\phi$ )<sup>2</sup> while it is proportional to D<sup>2</sup> for a  ${}^{P}\chi^{\rm EH}_{ijk}$  term. In general, the effective current amplitudes for the two effects should be added together to form the total current for frequency doubling. Thus

$$J_{T} = {}^{Q}J_{eff}^{EE} + {}^{P}J_{eff}^{EH}$$
$$= -2 \omega \left[ (\frac{iD}{z^{\circ}} + 2k^{\circ}A) + 2k^{\circ}B \cos 4\phi \right].$$

The experimental data plotted in Figure 14 and Fourier analysed in section (4-5) indicated that the frequency doubling in NiSO<sub>4</sub>.6 H<sub>2</sub>O was essentially independent of the angle  $\phi$ . The maximum value of  $\left|\frac{2Bk^{\circ}}{\frac{1D}{z^{\circ}} + 2k^{\circ}A}\right|$  permitted by the data is O.1. These results suggest

that the observed frequency doubling in NiSO<sub>4</sub>.6 H<sub>2</sub>O is a magnetic dipole effect due to an induced polarization  $P_i(2\omega) = {}^P \chi_{ijk}^{EH} E_j(\omega)$ H<sub>k</sub>( $\omega$ ). The electric quadrupole process is also consistent with the data for the special case that B = o, which is equivalent to the relation

 $^{Q}\chi_{1212}^{EE} = \frac{1}{2} (^{Q}\chi_{1111}^{EE} - ^{Q}\chi_{1122}^{EE})$ .

Table	V
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Effective Currents for Frequency Doubling in  ${\rm NiSO}_{4*}6~{\rm H_2O}$ 

Susceptibility	J <sub>eff</sub>	$\Phi$
$\overset{ extsf{p}}{ ilde{ ille} ilde{ ilde{ ilde{ ilde{ illed{ ilde{ ilde{ ille{ ille{ ille{ ille{ ille{ illet{ ille{ illet{ illet{ illet{ illet{ illet{ illet{ ille{ ille{ ille{ ille{ $	o	o
Ç <sup>EE</sup> Xijk <i>l</i>	- 4wx°T∮	A*B cos 4∳
${}^{\mathrm{P}}\!\!\chi^{\mathrm{EH}}_{\mathtt{ijk}}$	- 2i 🔐 T 🖗	D
M <sub>Z</sub> EE Mlk	O	o

## With OO-E Phase Matching

 $T = E^{o^2} e^{2i(\vec{k}^\circ \cdot \vec{r} - \omega t)}$   $A = \sin(\theta + \alpha_2) \cos \theta \frac{Q \chi^{\text{EE}}}{3311} - \sin \theta \cos(\theta + \alpha_2) \frac{Q \chi^{\text{EE}}}{1122} - B$   $B = \frac{1}{4} \sin \theta \cos(\theta + \alpha_2) \left[ \frac{Q \chi^{\text{EE}}}{1111} - \frac{Q \chi^{\text{EE}}}{1122} - 2 \frac{Q \chi^{\text{EE}}}{1212} \right]$   $C = \sin(\theta + \alpha_2) \cos \theta \frac{P \chi^{\text{EH}}}{312} - \sin \theta \cos(\theta + \alpha_2) \frac{P \chi^{\text{EH}}_{123}}{123}$ 

There is, of course, no basic reason why this relation among the susceptibility coefficients should hold, but one cannot exclude such a fortuitous condition.

It is interesting to note that no non-phase matched electric dipole frequency doubling due to the susceptibility  ${}^{P}\chi_{123}^{EE}$  was observed in NiSO<sub>4</sub>.6 H<sub>2</sub>O. It is possible therefore to put an upper limit on the value of  ${}^{P}\chi_{123}^{EE}$ . Consider the case of an E-ray at the fundamental frequency producing an O-ray at the doubled frequency. For non-phase matching, the second harmonic intensity in an absorbing crystal is given by equation (2-8). If it were possible to phase match, then the intensity would be given by equation (2-11). Taking the ratio of the two expressions it can be shown that

$$\frac{S(n_1^{e} = n_2^{o} = n)}{S(n_1^{e} \neq n_2^{o})} \approx \frac{1}{4} \frac{(n_1^{e} + n_2^{o})^2}{n_2^{o}n} \cdot \frac{k^2(n_1^{e} - n_2^{e})^2}{1 + \sinh^2 \xi \ell} \cdot \frac{\sinh^2 \xi \ell}{\xi^2} \sim 5 \times 10^{4}$$

for the NiSO<sub>4.6</sub> H<sub>2</sub>O platelet used in the relative magnitude experiments reported in section (4-7). In the calculation, it was assumed that  $n_1^{e} - n_2^{o} = .04$  and anisotropy in the absorption coefficients was neglected. The minimum non-phased matched radiation that would have been detected is

$$\frac{S(n_1^{e} \neq n_2^{o})}{S_1} = 10^{-9}$$

where  $S_1$  is the intensity of the second harmonic generated in the KDP platelet used in section (4-7). Using  $S(n_1^e = n_2^o = n) = 5 \times 10^4$  $S(n_1^e \neq n_2^o)$  and a calculation similar to those for the relative amplitudes in section (4-7), it can be estimated that  $\stackrel{P}{\sim}_{123} \stackrel{\text{EE}}{\underset{123}{}}$  in NiSO<sub>4</sub>.6 H<sub>2</sub>O is less than  $\frac{1}{25}$  the value of  ${}^{P}\chi {}^{EE}_{213}$  in KDP. The result is not too surprising since Kleinman's symmetry condition (27) requires  ${}^{P}\chi {}^{EE}_{123}$ to be zero in lossless, dispersionless materials belonging to the 422 point group. Unfortunately, the effectiveness of  ${}^{P}\chi {}^{EE}_{123}$  for frequency doubling is reduced so much by absorption and non-phase matching that a sensitive check of Kleinman's symmetry condition is not possible in NiSO<sub>4</sub>.6 H<sub>2</sub>O.

#### (5-3) Frequency Doubling in Calcite

Although frequency doubling in calcite has been observed by others (6) the results reported in section (4-5) are apparently the first on the azimuthal dependence. In the initial work on calcite the frequency doubling was attributed to an electric quadrupole effect, and it was on this basis that Pershan (26) calculated an (A+B sin  $3\phi$ )<sup>2</sup> dependence for the frequency doubling. Later however magnetic dipole effects were also indicated as a possible source for the frequency doubling (25). The relevant tensor elements for frequency doubling are listed in Table VI: and the azimuthal dependences for each are calculated in the Appendix following the approach given in section (2-5). A summary of the results is given in Table VII. Since both  $Q_{ij}$  =  ${}^{Q}\chi_{ijkl}^{EE}E_{k}E_{k}$  and  $P_{i} = {}^{P}\chi_{ijk}^{EH}E_{j}H_{k}$  give the same functional form for the azimuthal dependence, there is no way. from the experimental data to determine which process is involved. One can conclude, however, that  $M_k = \frac{M}{\chi} \chi_{mlk}^{EE} E_m E_l$  cannot solely be responsible for the frequency doubling in calcite since in that case it should show a (G sin  $3\phi$ )<sup>2</sup> azimuthal dependence.

Table	VI
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## The Frequency Doubling Susceptibilities in Calcite



jk	11	22	33	23	32	13	31	12	21
1	111	-111	0	123	132	0	0	0	0
2	0	0	0	0	0	-123	-132	-111	-111
3	0	0	0	0	0	0	0	312	-312

 $^{M}\chi_{m\ell k}^{EE}$  = (m $\ell k$ )

2k	11	22	33	23	32	13	31	12	21
m 1 2		<u>-111</u> 0	000	000	132 0	0	0 -132	0 -111 1 32	0 -111 -132

 $^{Q} \chi^{\text{EE}}_{ijkl}$  = (ijkl)

k@	11	22	33	23	32	13	31	12	21
11	1111	1122	1133	1123	1123	0	0	0	0
22	1122	1111	1133	-1123	-1123	0	0	0	0
33	3311	3311	3333	0	0	0	. 0	0	0
23	231.1	-2311	0	1313	<u>ر ار ۲</u>	0	0	0	.0
32	2311	-2311	0	E L SL S	1313		1 21 2	0	0
77	0	0	0	0	-0	<u>ز</u> لزلا د اد ا	1 21 2	11 2211	2211
	0	0		0		1102	1102	1212	1212
21	0	0	0	0	0	1123	1123	1212	1212

 $(1212) = \frac{1}{2} [(1111) - (1122)]$ 

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#### Table VII

## Effective Currents for Frequency Doubling in Calcite

Susceptibility	J <sub>eff</sub>	₽
PX <sup>EE</sup> ijk	0	o
QX <sup>EE</sup> ijke	- 4ωk° Τ∮	$A + B \sin 3\phi$
${}^{\mathrm{P}}\chi^{\mathrm{EH}}_{\mathtt{i}\mathtt{j}\mathrm{k}}$	- 2i $\frac{\omega}{z^{\circ}}$ T $\oint$	$D + F \sin 3\phi$
$^{M}\chi_{mlk}^{EE}$	2i c k°T∮	G sin 3 <i>p</i>

## With OO-E Phase Matching

 $T = E^{o^2} e^{2i(\vec{k}^{\circ} \cdot \vec{r} - \omega t)}$ A = sin( $\theta + \alpha_2$ ) cos  $\theta \, {}^{\mathbb{Q}} \chi_{3311}^{\mathbb{E}\mathbb{E}}$  - sin  $\theta \, \cos(\theta + \alpha_2) \, {}^{\mathbb{Q}} \chi_{1122}^{\mathbb{E}\mathbb{E}}$  $B = \cos(2\theta + \alpha_2) \sqrt[Q]{\chi_{2311}^{EE}}$  $D = \sin(\theta + \alpha_2) \cos \theta \overset{P}{\times} \overset{EH}{_{312}} - \sin \theta \cos(\theta + \alpha_2) \overset{P}{\times} \overset{EH}{_{123}}$  $F = -\cos(\theta + \alpha_2)\cos\theta P \chi_{111}^{EH}$  $G = \cos \alpha_2 \chi_{111}^{\text{EE}}$ 

The observation of weaker frequency doubling in calcite with OE-E phase matching relative to that obtained with OO-E indicates that the amplitude for second harmonic generation has decreased with OE-E phase matching. However, this fact does not allow a separation of the electric quadrupole and magnetic dipole effects in calcite. A summary of the effective currents with OE-E phase matching, as calculated in the Appendix, is given in Table VIII. The same azimuthal dependence is to be expected regardless of the origin of the effect. Hence a measurement of the azimuthal dependence with OE-E phase matching in calcite is not particularly interesting.

## Table VIII

## Effective Currents for Frequency Doubling in Calcite

Susceptibility	J <sub>eff</sub>	₽
${}^{P}\chi_{ijk}^{EE}$	0	0
<sup>Q</sup> X <sup>EE</sup> ijkl	$-2\omega(k^{\circ}*k^{e})T \oint$	A cos 3 ø
${}^{\mathrm{P}}\!\chi^{\mathrm{EH}}_{\mathtt{i}\mathtt{jk}}$	-2i $\frac{\omega}{z^{\circ}}$ T $\oint$	B cos 3¢
${}^{\rm M}\chi^{\rm EE}_{{ m m}{ m lk}}$	i c(k°*k <sup>e</sup> )T∮	D cos 3¢

## With OE-E Phase Matching

$$A = 2 \cos(\theta + \alpha_2) \sin(\theta + \alpha_1) \sin \theta \, \overset{Q}{\chi}_{1123}^{\text{EE}}$$
$$- 2 \cos(2\theta + \alpha_2) \cos (\theta + \alpha_1) \, \overset{Q}{\chi}_{2311}^{\text{EE}}$$
$$B = \cos(\theta + \alpha_2) \, \left[ 1 + \sin(\theta + \alpha_1) \right] \sin \theta \, \overset{P}{\chi}_{111}^{\text{EH}}$$
$$D = -2 \cos(\theta + \alpha_1) \cos \alpha_2 \, \overset{M}{\chi}_{111}^{\text{EE}}$$

 $T = E^{o}E^{e} e^{2i} (\bar{k}^{o} + \bar{k}^{e}) \cdot \bar{r} - \omega t)$ 

#### CHAPTER VI

#### CONCLUSIONS

The theory of slow Q-switching (40,41) was used to explain the appearance of multipulsing in a rotating prism Q-spoiled laser. The results indicate that the prime consideration in choosing a crystal for this type of Q-switch is maximum optical homogeneity and hence shortest switching time. This should be compared with the usual criterion of lowest threshold for laser oscillation in judging the worth of a laser crystal. The agreement between the experimental results and the theory of slow Q-switching was qualitative in nature but a more quantitative comparison would be desirable. Since the experimental results depend strongly on optical quality, there is little hope that such a comparison can be made using a  $Nd^{3+}$ :CaWO<sub>L</sub> Q-spoiled laser. The situation is different for a Nd-glass Q-spoiled laser in which optical imperfections are essentially non-existent. Such a quantitative investigation is now being carried out by Hill (45). Information on the effects of the life time of the laser transition's terminal level can be obtained.

The study of frequency doubling in NiSO<sub>4</sub>.6 H<sub>2</sub>O has indicated that the source of doubled frequency is an induced polarization  $P_i = {}^{P} \chi_{ijk}^{EH} E_j H_k$ , although the possibility of a contribution, in whole or in part, from  $Q_{ij} = {}^{Q} \chi_{ijk\ell}^{EE} E_k E_\ell$  cannot be completely excluded.

Three separate experimental observations support this conclusion. Firstly since the doubled frequency is an E-ray whose source at the fundamental frequency is an O-ray, the frequency doubling is not electric Secondly, the amplitude for frequency doubling is 1000 times dipole. smaller than in KDP while it is only 4 times greater than in calcite. Thus a nonlinear effect of higher order than electric dipole is implied. Finally the frequency doubling was found to be independent of the azimuthal angle  $\phi$  suggesting  $P_i = \frac{P \chi_{ijk}^{EH}}{E_{ijk}} E_{jk}$  as the doubled frequency As mentioned previously, the azimuthal dependence does not source. permit an absolutely unambiguous separation of the effects of  ${}^{\mathrm{P}}\!\chi^{\mathrm{EH}}_{\mathrm{ijk}}$ and  $\chi_{ijk\ell}^{EE}$  in NiSO<sub>4</sub>.6 H<sub>2</sub>O since the  $\phi$  dependence due to the latter can be reduced to a constant by setting the coefficient. B. of the  $\cos 4\phi$  term equal to zero. Since the fortuitous condition B = o, or  $\chi_{1212}^{\text{EE}} = \frac{1}{2} \left( \chi_{1111}^{\text{EE}} - \chi_{1122}^{\text{EE}} \right)$ , is highly improbable, it would be of interest to reduce the maximum value of B permitted by the experimental data. In this work. B was shown to be at least 10 times smaller than the constant term. An improved upper limit should be possible if the 10 to 15% rms deviations in the data could be reduced to the 4% uncertainty obtained in frequency doubling experiments with identical geometries for both monitor and sample crystal (21). The desired results might be obtained by using two cleaved platelets of NiSO4.6 H2O one as a monitor and the other as the sample crystal for the azimuthal dependence measurements. For the greatest signal strength the path length through the crystals should be 0.12 cm the thickness for optimum doubled frequency production.

The results presented in this work have not indicated any microscopic origin for the frequency doubling in NiSO4.6 H2O. Some experiments with this purpose will now be proposed. Since nickel is a magnetic atom, it would be interesting to see if the presence of the nickel ion is a requirement for the observed phenomena. A study of the magnitude and the azimuthal dependence of the frequency doubling in the isomorphs NiSe04.6 H20, ZnSe04.6 H20 and CoS04.6 H20 might show the effects of atomic substitution on the susceptibilities. Further information on the mechanism of the frequency doubling process in  $NiSO_{40}6H_2O$  could be obtained from a measurement of the dispersion in the nonlinear susceptibility. If it does not vary much with frequency a high frequency source for the susceptibility is indicated. Unfortunately, the presence of absorption makes dispersion experiments in NiSO4.6 H\_O difficult. However, one possibility is to use as a source the high intensity radiation at 0.53µm obtained from an efficient second harmonic generator such as KDP or lithium meta niobate and Nd-glass laser. The frequency doubling in NiSO4.6 H<sub>2</sub>O would then be from the green into the ultraviolet. By extrapolating Töpse and Christiansen's refractive index data type 00-E phase matching appears to be still possible at these frequencies.

The absence of non-phase matched radiation due to  $\mathcal{P}_{123} \overset{\text{EE}}{}_{123}$  provided a check on Kleinman's symmetry condition (27),  $\mathcal{P}_{123} \overset{\text{EE}}{}_{123} = 0$ , in NiSO<sub>4</sub>.6 H<sub>2</sub>O. A violation of the condition would have indicated a low frequency mechanism for the electric dipole doubling. However, since it is estimated that  $\mathcal{P}_{123} \overset{\text{EE}}{}_{123}$  is 1/25 or less  $\cdot$  than  $\mathcal{P}_{123} \overset{\text{EE}}{}_{123}$  in KDP, the test is not very sensitive. If OE-E phase matching were permitted, a more sensitive test would be possible since the amplitude for electric dipole frequency doubling is no longer zero as with OO-E phase matching. However, a search for OE-E phase matching was unsuccessful, probably due to the lack of sufficient birefringence.

Another extension of the experiments in NiSO<sub>4</sub>.6  $H_2O$  would be to apply a magnetic field and look for magnetic field-induced second harmonic generation. The effect has not yet been observed. Since the susceptibility for this effect is a 4th order axial tensor, its value is zero in centrosymmetric crystals. Hence it is only observable in those crystals for which symmetry conditions also allow electric dipole frequency doubling. The latter would probably overwhelm any magnetic fieldinduced frequency doubling. As has been shown, this would not be the case for the noncentrosymmetric crystals like NiSO<sub>4</sub>.6 H<sub>2</sub>O which have 422 symmetry. This experiment would be the magnetic analog of the experiment on electric field-induced doubling in calcite (6).

The measurements on the azimuthal dependence in calcite showed that the data are consistent with an  $(A + B \sin 3 \phi)^2$  variation, although the presence of the cos  $6\phi$  term was not observed. The results, however, do not allow a distinction to be made between the electric quadrupole and magnetic dipole effects. An attempt to observe the  $(D \cos 3 \phi)^2$  azimuthal dependence with OE-E phase matching was not carried out since it would not permit a separation of the two effects either.

The work in this thesis has demonstrated the possible use of the azimuthal dependence for distinguishing between the higher order terms in frequency doubling. The method is limited in its application, but is not restricted just to crystals with 422 symmetry. For example, the

negative uniaxial crystals with 4/mmm symmetry and 00-E phase matching have the same functional form for the azimuthal dependence of the electric quadrupole and magnetic dipole effects as do the 422 type crystals. However, if OE-E type phase matching is allowed, only quadrupole effects would be possible. In 4mm type uniaxial negative crystals. electric dipole frequency doubling can occur with OO-E phase matching. but only electric quadrupole doubling is possible with OE-E phase match-In addition, there is the possibility of measuring the ratio ing. between electric dipole and electric quadrupole effects in the same crystal to see if they have the same mechanism for the frequency doubling process. A study of the tables given in the Appendix and the calculation of a similar set for positive uniaxial crystals, will indicate the symmetries in which the azimuthal dependence can be used to separate the higher order nonlinear effects.

#### APPENDIX

#### THE AZIMUTHAL DEPENDENCE OF FREQUENCY DOUBLING IN CRYSTALS

The purpose of this Appendix is to present the calculations of the azimuthal dependence for electric dipole, magnetic dipole, and electric quadrupole frequency doubling in the three uniaxial crystal classes - tetragonal, trigonal, and hexagonal. The calculations have been carried out for both 00-E and OE-E type phase matching in uniaxial negative crystals.

It will be assumed that the applied fields are plane waves propagating through the crystal in the phase matched direction  $\bar{n}$  where

$$\bar{n} = \begin{bmatrix} \sin \theta \cos \phi \\ \sin \theta \sin \phi \\ \cos \theta \end{bmatrix}.$$

The optic axis has been taken in the z-axis direction. The angle  $\theta$  is measured from the optic axis to the direction of propagation, while  $\phi$ is the angle between the crystallographic x axis and the principal plane. The O-ray fields will be written as

$$\tilde{E}^{\circ}(\omega) = \tilde{o} E^{\circ} e^{i(\tilde{k}^{\circ} \cdot \tilde{r} - \omega t)}$$
  
and  $H^{\circ}(\omega) = \tilde{h}^{\circ} H^{\circ} e^{i(\tilde{k}^{\circ} \cdot \tilde{r} - \omega t)}$ 

where

$$\bar{o} = \begin{bmatrix} \sin\phi \\ -\cos\phi \\ 0 \end{bmatrix} \qquad \bar{h}^{\circ} = \begin{bmatrix} \cos\theta \cos\phi \\ \cos\theta \sin\phi \\ -\sin\theta \end{bmatrix}$$

and  $E^{\circ} = z^{\circ} H^{\circ}$  where  $z^{\circ}$  is the impedance of the medium. Similarly the E-ray is given by

$$\tilde{\mathbf{E}}^{\mathbf{e}}(\omega) = \tilde{\mathbf{e}}_{\mathbf{l}} \mathbf{E}^{\mathbf{e}} \mathbf{e}^{\mathbf{i}(\bar{\mathbf{k}}^{\mathbf{e}}\cdot\bar{\mathbf{r}}-\omega\mathbf{t})}, \quad \tilde{\mathbf{H}}^{\mathbf{e}}(\omega) = \tilde{\mathbf{h}}^{\mathbf{e}} \mathbf{H}^{\mathbf{e}} \mathbf{e}^{\mathbf{i}(\bar{\mathbf{k}}^{\mathbf{e}}\cdot\bar{\mathbf{r}}-\omega\mathbf{t})}$$

where

$$E^e = z^e H^e$$

and

$$\bar{e}_{1} = \begin{bmatrix} -\cos(\theta + \alpha_{1})\cos\phi \\ -\cos(\theta + \alpha_{2})\sin\phi \\ \sin(\theta + \alpha_{1}) \end{bmatrix} \qquad \bar{h}^{e} = \begin{bmatrix} \sin\phi \\ -\cos\phi \\ o \end{bmatrix}.$$

The quantity  $\alpha_1$  is the angle between the direction of Poynting's vector for the E-ray and its wave normal  $\overline{k}^e$ . Its value can be found from

 $\tan \alpha_{1} = \frac{\begin{pmatrix} 1 & -\frac{n_{1}^{o^{2}}}{n_{1}^{e^{2}}} \end{pmatrix} \tan \theta}{1 + \frac{n_{1}^{o^{2}}}{n_{1}^{e^{2}}} \tan^{2}\theta}$ 

As the fields propagate through the medium, they induce a source current at the doubled frequency. Not all of the source current is effective in second harmonic generation, but only the component along the direction of the electric vector for the E-ray at the doubled frequency. It is given by

$$J_{eff}(2\omega) = \bar{e}_2 \cdot \bar{J}(2\omega) = e_{2i} J_i(2\omega)$$

where

$$\overline{J}(2\omega) = \frac{\partial \overline{P}(2\omega)}{\partial t} + c \,\overline{\nabla} X \,\overline{M}(2\omega) - \frac{\partial}{\partial t} (\overline{\nabla} . \overline{Q})$$

and

$$\bar{e}_{2} = \begin{bmatrix} -\cos(\theta + \alpha_{2})\cos\phi \\ -\cos(\theta + \alpha_{2})\sin\phi \\ \sin(\theta + \alpha_{2}) \end{bmatrix}.$$

As for  $\alpha_1$ , there is an analogous expression for  $\alpha_2$ ,

$$\tan \alpha_2 = \frac{\left(1 - \frac{n_1^{0^2}}{n_1^{e^2}}\right) \tan \theta}{1 + \frac{n_1^{0^2}}{n_1^{e^2}} \tan^2 \theta}$$

The second harmonic intensity will be proportional to  $J_{eff}^{2}(2\omega)$ . The problem now is to evaluate  $J_{eff}$  for each of the induced moments.

(a) 
$$P_i(2\omega) = {}^P \chi_{ijk}^{EE} = E_j(\omega) = k(\omega).$$

For the case of OO-E phase matching,

$$E_{j}(\omega) E_{k}(\omega) = o_{j}o_{k} E^{o^{2}} e^{2i(\bar{k}^{\circ}\cdot\bar{r} - \omega t)}$$

Hence the effective current is

$$J_{eff} = -2i\omega E^{o^2} \oint e^{2i(\bar{k}^{\circ}.\bar{r} - \omega t)}$$
where the quantity  $\oint contains$  the azimuthal dependence and is given by  $\oint = e_{2i} \circ_j \circ_k \stackrel{P}{\sim}_{ijk} \stackrel{EE}{ijk}$ . On the other hand, for OE-E type phase matching,  $E_j(\omega) E_k(\omega) = (\circ_j e_{1k} + e_{1j} \circ_k) E^{\circ} E^{e} e^{i \left[ (\bar{k}^{\circ} + \bar{k}^{e}) \cdot \bar{r} - 2\omega t \right]}$ 

and the effective current is given by

$$J_{eff} = -2i\omega \oint \mathbb{E}^{\circ} \mathbb{E}^{e} e^{i} \left[ (\bar{k}^{\circ} + \bar{k}^{e}) \cdot \bar{r} - 2\omega t \right]$$
where  $\oint = e_{2i} (\circ_{j} e_{1k} + e_{1j} \circ_{k}) \mathcal{P}_{ijk}^{EE}$ .  
(b)  $Q_{ij} = Q \chi_{ijk\ell}^{EE} \mathbb{E}_{k} \mathbb{E}_{\ell}$ .  
Since  $\bar{J} = -\frac{\partial}{\partial t} (\bar{\nabla} \cdot \bar{Q})$ ,  
 $J_{eff} = \bar{e}_{2} \cdot \bar{J} = -\frac{\partial}{\partial t} e_{2i} (\partial_{j} Q_{ij})$   
 $= -\frac{\partial}{\partial t} e_{2i} \partial_{j} (Q \chi_{ijk\ell}^{EE} \mathbb{E}_{k} \mathbb{E}_{\ell})$ .

For OO-E type phase matching.

$$J_{eff} = -4\omega k^{\circ} E^{\circ} \int e^{2i(\vec{k}^{\circ} \cdot \vec{r} - \omega t)}$$

where  $\oint = e_{2i} n_j o_k o_l \chi_{ijkl}^{EE}$ ,

and for OE-E phase matching

$$J_{eff} = -2\omega(k^{\circ} + k^{e}) E^{e} E^{\circ} \oint e^{i} \left[ (\bar{k}^{\circ} + \bar{k}^{e}) \cdot \bar{r} - 2\omega t \right]$$

where

$$\Phi = e_{2i} n_{j} (o_{k} e_{1\ell} + e_{1k} o_{\ell}) \chi^{EE}_{ijk\ell}$$

(c) 
$$P_i = \gamma \chi_{ijk}^{EH} E_{jk}^{H}$$

For OO-E phase matching

$$E_{j} H_{k} = o_{j} h_{k}^{o} E^{o} H^{o} e^{2i(\vec{k}^{o} \cdot \vec{r} - \omega t)}$$
$$= o_{j} h_{k}^{o} \frac{E^{o}}{z^{o}} e^{2i(\vec{k}^{o} \cdot \vec{r} - \omega t)}$$

Hence the effective current is

$$J_{eff} = -2i \frac{\omega}{z^{\circ}} = E^{o^2} \oint e^{2i(\bar{k}^{\circ} \cdot \bar{r} - \omega t)}$$

where

$$\Phi = e_{2i} \circ_{j} h_{k} \gamma_{ijk}^{EH}$$

For OE-E phase matching

$$E_{j}H_{k} = (\circ_{j}h_{k}^{e} E^{\circ} H^{e} + e_{lj}h_{k}^{\circ} E^{e} H^{\circ}) e^{i} \left[ (\bar{k}^{\circ} + \bar{k}^{e}).\bar{r} - 2\omega t \right]$$
$$= \left[ \frac{\circ_{j}h_{k}^{e}}{z^{e}} + \frac{e_{lj}h_{k}^{\circ}}{z^{\circ}} \right] E^{\circ} E^{e} e^{i} \left[ (\bar{k}^{\circ} + \bar{k}^{e}).\bar{r} - 2\omega t \right].$$

At phase matching  $z^e = z^o$ , and the effective current is

$$J_{eff} = -2i \frac{\omega}{z^{\circ}} E^{\circ} E^{\circ} \Phi_{e}^{i} \left[ (\bar{k}^{\circ} + \bar{k}^{e}) \cdot \bar{r} - 2\omega t \right]$$

where

(d) 
$$M_{k}(2\omega) = {}^{M}\chi_{mk}^{EE} E_{m}(\omega) E_{\ell}(\omega)$$
,

The induced current is

$$J_{i} = c \left( \overline{\nabla} \times \overline{M} \right)_{i} = c \epsilon^{ijk} \partial_{j} M_{k}$$

where  $e^{ijk}$   $\begin{cases} * l \text{ for cyclic permutations of } i, j, k \\ - l \text{ for anticyclic permutations of } i, j, k \\ o \text{ for two or more } i, j, k equal. \end{cases}$ 

Hence the effective current is

$$J_{\text{eff}} = c e_{2i} \epsilon^{ijk} \partial_j \chi^{\text{EE}}_{m\ell k} E_m E_{\ell}.$$

For OO-E phase matching this reduces to

$$J_{eff} = 2i c k^{\circ} E^{\circ} \Phi e^{2i(\vec{k}^{\circ} \cdot \vec{r} - \omega t)}$$

where

$$\oint = e_{2i} n_j \epsilon^{ijk} \circ_m \circ_\ell \qquad \stackrel{M}{\sim} \chi_{m\ellk}^{EE}$$

and for OE-E phase matching

$$J_{eff} = ic(k^{\circ} + k^{e}) E^{\circ} E^{e} \oint e^{i} \left[ (\bar{k}^{\circ} + k^{e}) \cdot \bar{r} - 2\omega t \right]$$

where

$$\Phi = e_{2i} n_j \epsilon^{ijk} (o_{\ell} e_{1m} + e_{1\ell} o_m) {}^{M} \chi_{\ell mk}^{EE}.$$

The summations implied in  $\overline{\Phi}$  have been evaluated in the crystal classes, tetragonal, trigonal, and hexagonal, for each of the 8 expressions derived above. This was accomplished with the aid of a review article by Birss (10) in which the crystal symmetry restrictions on the

coefficients of both polar and axial tensors are listed. The results are presented in the following order. First in Table A-I, A-II, A-III, and A-IV the quantities  $e_{2i} \circ_{j} \circ_{k}$ ,  $e_{2i} n_{j} \circ_{k} \circ_{\ell}$ ,  $e_{2i} \circ_{j} h_{k}^{\circ}$  and  $\mathcal{E}^{ijk}_{\mathcal{E}_{k}n_{j}} \circ_{\ell} \circ_{m}$  for OO-E type phase matching are listed. These are followed by Tables A-V, A-VI, A-VII, A-VIII giving the sums  $\overline{\Phi} = e_{2i} \circ_{j} \circ_{k}^{P} \chi_{ijk}^{EE}$ ,  $e_{2i} n_{j} \circ_{k} \circ_{\ell}^{Q} \chi_{ijk\ell}^{EE}$ ,  $e_{2i} \circ_{j} h_{k}^{\circ} \chi_{ijk}^{EH}$ , and  $e_{2i} n_{j} \mathcal{E}^{ijk} \circ_{m} \circ_{\ell}^{M} \chi_{m\ell k}^{EE}$ . In an analogous fashion, the next set of tables contains the results of the calculations for OE-E phase matching. Thus the quantities  $e_{2i} (\circ_{j} e_{1k} * e_{1j} \circ_{k})$ ,  $e_{2i} n_{j} (\circ_{k} e_{1\ell} + e_{1k} \circ_{\ell})$ ,  $e_{2i} (\circ_{j} h_{k}^{e} + e_{1j} h_{k}^{\circ})$ , and  $e_{2i} n_{j} \mathcal{E}^{ijk} (\circ_{\ell} e_{1m} + \circ_{m} e_{1\ell})$  are listed in Tables A-IX, A-XI and A-XII respectively, while the sums  $\overline{\Phi} = e_{2i} (\circ_{j} e_{1k} + e_{1j} \circ_{k}) {}^{P} \chi_{ijk}^{EE}$ ,  $e_{2i} n_{j} (\circ_{k} e_{1\ell} + e_{1k} \circ_{\ell}) {}^{Q} \chi_{ijk\ell}^{EE}$ ,  $e_{2i} (\circ_{j} h_{k}^{e} + e_{1j} h_{k}^{\circ}) {}^{P} \chi_{ijk}^{EE}$ ,  $e_{2i} n_{j} (\circ_{k} e_{1\ell} + e_{1k} \circ_{\ell}) {}^{Q} \chi_{ijk\ell}^{EE}$ ,  $e_{2i} (\circ_{j} h_{k}^{e} + e_{1j} h_{k}^{\circ}) {}^{P} \chi_{ijk}^{EE}$ ,  $e_{2i} n_{j} (\circ_{\ell} e_{1m} + e_{1\ell} \circ_{\ell}) {}^{Q} \chi_{ijk\ell}^{EE}$ ,  $e_{2i} (\circ_{j} h_{k}^{e} + e_{1j} h_{k}^{\circ}) {}^{P} \chi_{ijk}^{EH}$  and  $e_{2i} n_{j} \mathcal{E}^{ijk} (\circ_{\ell} e_{1m} + e_{1\ell} \circ_{\ell}) {}^{Q} \chi_{ijk\ell}^{EE}$ ,  $e_{2i} (\circ_{j} h_{k}^{e} + e_{1j} h_{k}^{\circ}) {}^{P} \chi_{ijk}^{EH}$  and  $e_{2i} n_{j} \mathcal{E}^{ijk} (\circ_{\ell} e_{1m} + e_{1\ell} \circ_{\ell}) {}^{Q} \chi_{m\ell k}^{EE}$ are given in Tables A-XIII. A-XIV, A-XV and A-XVI.

Table	A-I:	The	Quantity	e o	,0,
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jk 1	11	22	33	23	32	13	31	12	21.
1	-C2 <sup>5<sup>2</sup>c</sup>	-0 <sub>2</sub> c <sup>3</sup>	0	0		C	) .	C2s	c <sup>2</sup>
2	-C2s3	-C <sub>2</sub> sc <sup>2</sup>	0	0		0		C <sub>2</sub> s	<sup>2</sup> c
3	525 <sup>2</sup>	S <sub>2</sub> e <sup>2</sup>	0	0		С	)	-S <sub>2</sub> s	c

 $S_2 = \sin(\theta + \alpha_2), C_2 = \cos(\theta + \alpha_2), s = \sin \phi, c = \cos \phi$ 

Table A-II: The Quantity ezinjokol

kl ij	11	22	33	23	32 13 31		31	12	21
11	-C <sub>2</sub> Ss <sup>2</sup> c <sup>2</sup>	-C <sub>2</sub> Sc <sup>4</sup>	0	0		0		C <sub>2</sub> Ssc <sup>3</sup>	
22	-C <sub>2</sub> Ss <sup>4</sup>	-C <sub>2</sub> Ss <sup>2</sup> c <sup>2</sup>	0	0		0		C <sub>2</sub> Ss <sup>3</sup> c	
33	S <sub>2</sub> Cs <sup>2</sup>	s <sub>2</sub> cc <sup>2</sup>	0	0		0		-S <sub>2</sub> Csc	
23	-C <sub>2</sub> Cs <sup>3</sup>	-0 <sub>2</sub> 0sc <sup>2</sup>	0	0		0		C <sub>2</sub> Cs <sup>2</sup> c	
32	S2Ss3	S <sub>2</sub> Ssc <sup>2</sup>	Q	0	0 0		-S <sub>2</sub> S	s c	
13	-020s <sup>2</sup> c	-c20c <sup>3</sup>	0	0	0 0		C <sub>2</sub> C	sc <sup>2</sup>	
31	S <sub>2</sub> Ss <sup>2</sup> c	S <sub>2</sub> Sc <sup>3</sup>	0	0		c c		-s <sub>2</sub> s	2 isc
12	-C <sub>2</sub> Ss <sup>3</sup> c	-C2Ssc <sup>3</sup>	0	0		0	-	C2S	2 2 s c
21	-C <sub>2</sub> Ss <sup>3</sup> c	-C2Ssc <sup>3</sup>	0	0		С	· ·	°2 <sup>S</sup>	2 2 s c

 $S_2 = \sin(\theta + \alpha_2), C_2 = \cos(\theta + \alpha_2), S = \sin\theta, C = \cos\theta, s = \sin\phi, c = \cos\phi$ 

jk i	11	22	33	23	32	13	31	12	21.
1	-C <sub>2</sub> Csc <sup>2</sup>	C <sub>2</sub> Csc <sup>2</sup>	0	-c2sc <sup>2</sup>	0	C <sub>2</sub> Ssc	0	-C2Cs <sup>2</sup> c	C <sub>2</sub> Cc <sup>3</sup>
2	-C <sub>2</sub> Cs <sup>2</sup> c	C <sub>2</sub> Cs <sup>2</sup> c	0	-C <sub>2</sub> Ssc	0	C2Ss <sup>2</sup>	0	-C <sub>2</sub> Cs <sup>3</sup>	C <sub>2</sub> Csc <sup>2</sup>
3	S <sub>2</sub> Csc	-S <sub>2</sub> Csc	0	S <sub>2</sub> Sc	0 -	-S <sub>2</sub> Ss	0	S <sub>2</sub> Cs <sup>2</sup>	-520c <sup>2</sup>

 $S_2 = \sin(\theta + \alpha_2), C_2 = \cos(\theta + \alpha_2), S = \sin\theta, C = \cos\theta, s = \sin\phi, c = \cos\phi$ 

Table A-III: The Quantity  $e \circ h^{O}$ 2i j k

				1 36	•
Table	A-IV:	The	Quantity	e_1	e <sub>2</sub> , n, o <sub>0</sub> o <sub>m</sub>

k Lm	11	22	33	23	32	13	31	12	21
l	-5 <sup>3</sup> cosa2	-sc <sup>2</sup> cosa <sub>2</sub>	0	0		0		s <sup>2</sup> c cos <sub>2</sub>	
2	s <sup>2</sup> c cos¢ <sub>2</sub>	c <sup>3</sup> cosoz	0	0		0		<b>-sc</b> <sup>2</sup> c	ಂತಳ್ಳ
3	0	0	0	0		0		0	

 $s = \sin \phi$ ,  $c = \cos \phi$ 

Table A-V The Quantity  $\Phi = e_{2i} o_j o_k \overset{P}{\times}_{ijk}^{EE}$ 

Crystal Class	Point Group	$\Phi$			
	4	A			
	4	-A cos $2\phi$ + B sin $2\phi$			
	Ц/т	0			
Tetragonal	422	0			
	Limm -	A			
	<b>4</b> 2m	B sin 2Ø			
	L1/mmm	0			
	3	A + D cos 3Ø + E sin 3Ø			
	3	0			
Trigonal	32	D cos $3\beta$			
	3m	A + E sin $3\emptyset$			
	3m	0			
	6	A			
	6	$D \cos 3\phi + E \sin 3\phi$			
	6/m	0			
Hexagonal	622	0			
	6mm	A			
	6m2	D cos 3Ø			
	6/mmm	0			

A =  $(311)S_2$ , B = -  $(312)S_2$ , D =  $(111)C_2$ , E = -  $(222)C_2$  $S_2 = \sin(\Theta + \sigma_2)$ ,  $C_2 = \cos(\Theta + \sigma_2)$ ,  $\stackrel{P}{\times} \stackrel{EE}{ijk} = (ijk)$ 

# Table A-VI The Quantity $\Phi = e_{2i}n_j o_k o_l \chi_{ijkl}^{EE}$

Crystal Class	Point Group	arPhi		
•	4, <del>I</del> r,	A + B cos $4\phi$ + D sin $4\phi$		
Tetragonal	4/m	•		
	422, 42m,	A + B cos lia		
	4mm, 4/mmm	A T D COS 40		
Trigonal	3, 3,	$E + F \cos 3\emptyset + G \sin 3\emptyset$		
	32, 3m,	F+ G sin 20		
	3m			
	6, <del>6</del> ,	D		
Hovagonal	6/m	Ь		
Herogonar	622, 6mm,	D		
	6m2, 6/mmm	Ľ.		

$$\begin{split} A &= S_2 C(3311) - C_2 S(1122) - B \\ B &= \frac{1}{4} C_2 S[(1111) - (1122) - 2(1212)] \\ D &= \frac{1}{2} C_2 S[(1112) + (1211)] \\ E &= S_2 C(3311) - C_2 S(1122) \\ F &= (1311) \cos (2\theta + \aleph_2) \\ G &= (2311) \cos (2\theta + \aleph_2) \\ S_2 &= \sin (\theta + \aleph_2), \ C_2 &= \cos (\theta + \aleph_2), \ S &= \sin \theta , \ C &= \cos \theta , \\ {}^Q \chi_{ijk\ell}^{EE} &= (ijk\ell) \end{split}$$

## Table A-VII The Quantity $\Phi = e_{2i}o_jh_k^{oP} \chi_{ijk}^{EH}$

Crystal Class	Point Group	arPhi		
	4, 4,	A		
Tot nocon a	Ц/m			
Teoragonar	422, 4mm,	Δ		
	<u>4</u> 2m <b>,</b> 4/mmm	A		
	3, 3	A * B cos 3Ø + D sin 3Ø		
Trigonal	32, 3m,	$\Lambda + D \sin 30$		
	3m			
	6, 7,	٨		
Verenenel	6/m	A		
nexagonar	622, 6mm,	٨		
	6∕mmm	A		

$$A = S_2C(312) - C_2S(123)$$
  

$$B = -C_2C(222)$$
  

$$D = -C_2C(111)$$
  

$$P_{ijk}^{EH} = (ijk)$$
  

$$S_2 = \sin(\Theta + \infty_2), \quad C_2 = \cos(\Theta + \infty_2)$$

		Tal	ble	€ A-VIII		
The	Quantity	$\overline{\Phi}$	8	e <sub>2i</sub> nje <sup>ij</sup>	<sup>k</sup> ol <sup>o</sup> m	$\mathbf{x}_{mlk}^{\mathrm{EE}}$

Crystal Class	Point Group	arPhi		
	4,五 4/m	0		
Tetragonal	422, 4mm, 42m, 4/mmm	0		
,	3, 3	A cos 3Ø + B sin 3Ø		
Trigonal	32, 3m, 3m	B sin 3Ø		
	6, 7 6/m	0		
Hexagonal	622, 6mm, Tm2, 6/mmm	0		

 $A = (222) \cos \alpha_2$   $B = (111) \cos \alpha_2$  $M \chi_{mlk}^{EE} = (mlk)$ 

Table A-	IX: The	Quantity	e <sub>2i</sub> (o <sub>i</sub> e <sub>1k</sub>	+	ejok)
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jk i	11	22	33	23	32	13	31	12	21
1	C <sub>2</sub> C <sub>1</sub> s c	- <sup>C</sup> 2 <sup>C</sup> 1 <sup>sc</sup>	0	°2 <sup>\$</sup> 1	c <sup>2</sup>	-c <sub>2</sub> s	lsc	- <sup>c</sup> 2	C <sup>1</sup> cc
2	C <sub>2</sub> C <sub>1</sub> ss	-c <sub>2</sub> c <sub>1</sub> ss	0	°2 <sup>S</sup> 1sc		-c <sub>2</sub> s	1 <sup>s<sup>2</sup></sup>	-c <sub>2</sub>	°₁s <u>c</u>
3	-S <sub>2</sub> C <u>1s</u>	S2C13	0	-s <sub>2</sub> s	J <sub>C</sub>	S <sub>2</sub> S	1 <sup>8</sup>	s <sub>2</sub>	°1 <u>°</u>

 $S_2 = \sin(\theta + \alpha_2), S_1 = \sin(\theta + \alpha_1), \underline{s} = \sin 2\theta, s = \sin \theta,$ 

 $C_2 = \cos (\theta + \alpha_2), C_1 = \cos (\theta + \alpha_1), \underline{c} = \cos 2\emptyset, c = \cos \emptyset$ 

Table	A-X:	The	Quantity	$e_{2i}n_i(o_k e_j)$	+	$e_{\gamma_{v}}o_{0})$
						TU T

. .

. .

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klij	11	22	33	23	32	13	31	12	21
11	C2C1SEC <sup>2</sup>	-C2C1 Sec2	0	<sup>C</sup> 2 <sup>S</sup> 1	Sc <sup>3</sup>	-c <sub>2</sub> s	1 <sup>Ssc<sup>2</sup></sup>	-c <sub>2</sub> c <sub>1</sub>	Se <sup>2</sup> c
22	C <sub>2</sub> C <sub>1</sub> Sss <sup>2</sup>	-C <sub>2</sub> C <sub>1</sub> Sss <sup>2</sup>	0	°2 <sup>S</sup> 1Ss <sup>2</sup> c		<sup>C</sup> 2 <sup>S</sup> 1 <sup>SS<sup>2</sup>c -<sup>C</sup>2<sup>S</sup>1<sup>SS<sup>3</sup></sup></sup>		-c <sub>2</sub> c <sub>1</sub>	Ss <sup>2</sup> c
33	-s <sub>2</sub> c <sub>1</sub> cs	S <sub>2</sub> C <sub>1</sub> C <u>s</u>	0	-S2S1Ce		-S <sub>2</sub> S <sub>1</sub> Cc S <sub>2</sub> S <sub>1</sub> Cs		s <sub>2</sub> c <sub>1</sub> c	c
23	C <sub>2</sub> C <sub>1</sub> Css	-C2C1Css	0	C <sub>2</sub> S <sub>1</sub> Csc		- <sup>C</sup> 2 <sup>S</sup> 1 <sup>C</sup> s <sup>2</sup>		-°2°1°sc	
32	-S2C1Sss	S2C1SES	0	-S_S	l <sup>Ssc</sup>	S2S1S52		S2C1S	sc
13	°2°1°5c	- <sup>C</sup> 2 <sup>C</sup> 1 <sup>C</sup> 5c	0	<sup>C</sup> 2 <sup>S</sup> 1	Cc <sup>2</sup>	-c <sub>2</sub> s	l <sup>Csc</sup>	-c <sub>2</sub> c <sub>1</sub>	Ccc
31	-S2C1SEC	S <sub>2</sub> C <sub>1</sub> Ssc	0	-s2s	1 <sup>Sc<sup>2</sup></sup>	S2S1	Ssc	S2C1S	c <u>c</u>
12	C <sub>2</sub> C <sub>1</sub> Sssc	-C2C1Sssc	0	<sup>C</sup> 2 <sup>S</sup> 1	Ssc <sup>2</sup>	-c <sub>2</sub> s	1 <sup>Ss<sup>2</sup>c</sup>	-c <sub>2</sub> c <sub>1</sub>	Sscc
21	C2C1 Sesc	-C2C1Sssc	0	<sup>C</sup> 2 <sup>S</sup> 1	Ssc <sup>2</sup>	-C <sub>2</sub> S	1 <sup>Ss<sup>2</sup>c</sup>	-c <sub>2</sub> c <sub>1</sub>	Cscc
S2 = 0 C2 = 0	$S_{2} = \sin(\theta + \alpha_{2}), S_{1} = \sin(\theta + \alpha_{1}), S = \sin\theta, \underline{s} = \sin 2\theta, s = \sin\theta$ $C_{2} = \cos(\theta + \alpha_{2}), C_{1} = \cos(\theta + \alpha_{1}), C = \cos\theta, \underline{c} = \cos 2\theta, c = \cos\theta.$								

jk i	11	22	33	23	32	13	31	12	21
l	<sup>C</sup> 2 <sup>C</sup> 1 <sup>Cc<sup>3</sup></sup>	°2°1°°°°	°2 <sup>S</sup> 1 <sup>Sc</sup>	-C <sub>2</sub> S <sub>1</sub> Csc	-C2C1Ssc	- <sup>C</sup> 2 <sup>S</sup> 1 <sup>Cc<sup>2</sup></sup>	-C <sub>2</sub> C <sub>1</sub> Sc <sup>2</sup>	°2°1°	sc <sup>2</sup>
	-c <sub>2</sub> s <sup>2</sup> c	-c <sub>2</sub> c <sup>3</sup>	:					• + C <sub>2</sub> s	c <sup>2</sup>
2	C <sub>2</sub> C <sub>1</sub> Csc <sup>2</sup>	°2°⊒°s <sup>3</sup>	C_S_Ss	-C <sub>2</sub> S <sub>2</sub> Cs <sup>2</sup>	-C <sub>2</sub> C <sub>1</sub> Ss <sup>2</sup>	-C <sub>2</sub> S <sub>1</sub> Csc	-C_C_Ssc	°2°1°	s <sup>2</sup> c
	-c <sub>2</sub> s <sup>3</sup>	-c <sub>2</sub> sc <sup>2</sup>						+ C <sub>2</sub> s	<sup>2</sup> c
3	-S <sub>2</sub> C <sub>1</sub> Cc <sup>2</sup>	-S <sub>2</sub> C <sub>2</sub> Cs <sup>2</sup>	-s_s_s 2 1	S S Cs 2 1	S_C_Ss 2 1	S S Cc 2 1	S_C_Sc 2 1	-5 C ( 2 1	Csc
	+ S <sub>2</sub> s <sup>2</sup>	+ 5 <sub>2</sub> c <sup>2</sup>						-S_sc	
S <sub>2</sub> = s	in.( $\theta + \alpha_2$	), S = si	$\ln (\theta + \propto 1)$	), S = sin	n <b>0, s=</b> ;	sin Ø			
$C_2 = c_1$	os ( $\theta + \alpha_2$	), $C_1 = cc$	$(\theta + \alpha_1)$	), $C = cos$	s θ, с = (	cos Ø.			

Table A-XI: The Quantity  $e_{2i}(o_jh_k^e + e_{1jk}h_k^o)$ 

Table A-XII:	The	Quantity	e <sub>2i</sub> n <sub>j</sub> e <sup>ijl</sup>	k(oleim	÷	elfom)
--------------	-----	----------	---	---------	---	--------

l.m k	11	22	33	23	32	13	31	12	21
1	C <sub>1</sub> ss cos∝2	-C <sub>1</sub> ss cos∝ 1- 2	0	S <sub>l</sub> sc c	os∝2	-S <sub>1</sub> s <sup>2</sup>	cosa 2	-C <sub>l</sub> sc	cosox
2	-C <sub>1</sub> sc cos∝2	C <sub>l</sub> sc cos x	0	-s <sub>l</sub> c² c	osa 2	S_sc l	co s oz	°₁cc	cos¢ 2
3	0	0	0	0	)	0		C	)

 $S_{1} = \sin (\theta + \alpha), \quad \underline{s} = \sin 2\beta, \quad \underline{s} = \sin \beta,$  $C_{1} = \cos (\theta + \alpha_{1}), \quad \underline{c} = \cos 2\beta, \quad \underline{c} = \cos \beta.$ 

#### Table A-XIII

Crystal Class	Point Group	$\Phi$
<del>d her so - , , , , , , , , , , , , , , , , , , </del>	4	A
	<u>1</u>	(A + B) cos 2Ø + D sin 2Ø
	4/m	· · · O · ·
Tetragonal	422	A
	Linna	0
	<u>4</u> 2m	(A + B) cos 2Ø
	4/mnum	0
	3	A + E sin $3\not p$ + F cos $3\not p$
	3	0
Trigonal	32	$A + E \sin 3\emptyset$
	3m	F cos 3Ø
	3m	0
	6	A
	6	E sin $3\emptyset$ + F cos $3\emptyset$
	6/m	0
Hexagonal	622	A
• · · · · ·	6mm	0
	6m2	E sin 3ø
	6/mmm	0

The Quantity  $\Phi = e_{2i}(o_j e_{1k} + e_{1j}o_k)^P \chi_{ijk}^{EE}$ 

 $\begin{aligned} &A = 2(123)C_{21}^{S}, \quad B = 2(312)S_{21}^{C}, \quad D = -2\left[S_{21}^{C}(311) + C_{21}^{S}(113)\right], \\ &E = 2(111)C_{21}^{S}, \quad F = 2(222)C_{21}^{S}, \quad \frac{P}{2} \underset{ijk}{\overset{EE}{\underset{ijk}{\overset{EE}{\atop_{ijk}}}} = (ijk), \\ &S_{2} = \sin\left(\theta + \alpha_{2}^{'}\right), \quad C_{2} = \cos\left(\theta + \alpha_{2}^{'}\right), \quad S_{1} = \sin\left(\theta + \alpha_{1}^{'}\right), \quad C_{1} = \cos\left(\theta + \alpha_{1}^{'}\right) \end{aligned}$ 

			Tabl	e a-xiv			
The	Quantity	$\Phi$	<sup>∞</sup> <sup>e</sup> 2	i <sup>n</sup> j(oke	1 <b>e +</b>	elkog)	$\chi^{\rm EE}_{\rm ijkl}$

Crystal Class	Point Group	$\Phi$			
	4, <u>ī</u> ,	A + B sin hØ + D cos hØ			
Tot magonal	4/m	· · · · · · · · · · · · · · · · · · ·			
Tentefour	422, 4mm,	P cin há			
	μ̃2m, μ/mmm	B SIN 49			
	<b>3,</b> 3	$E + F \sin 3\phi + G \cos 3\phi$			
Trigonal	32, 3m,	6 003 30			
	3m				
	6, 6	а Т			
Hexagonal	6/m	24			
	622, 6mm,	0			
	6m2, 6/mmm	U			

$$\begin{split} A &= 2S_{1}(1323) \cos (2\theta + \alpha_{2}) + C_{2}C_{1}S[(1211) - (1112)] \\ B &= \frac{1}{2}C_{2}C_{1}S[(1111) - (1122) - 2(1212)] \\ D &= -C_{2}C_{1}S[(1211) + (1112)] \\ E &= 2S_{1}(1323) \cos (2\theta + \alpha_{2}) + 2C_{2}C_{1}S(1211) \\ F &= 2C_{1}(1311) \cos (2\theta + \alpha_{2}) - 2C_{2}S_{1}S(1113) \\ G &= 2C_{2}S_{1}S(1123) - 2C_{1}(2311) \cos (2\theta + \alpha_{2}) \\ S_{2} &= \sin (\theta + \alpha_{2}), C_{2} &= \cos (\theta + \alpha_{2}), S_{1} &= \sin (\theta + \alpha_{1}), C_{1} &= \cos (\theta + \alpha_{1}), \\ Q \times_{ijkl}^{EE} &= (ijkl) \end{split}$$

## Table A-XV

Crystal Class	Point Group	$\overline{\Phi}$
	4, <del>4</del> ,	A
Tetragonal	Ц/m	
I GOL OGUMAL	422, 4mm,	0
	<u>4</u> 2m, 4/mmm	U
	3, 3	$A + B \sin 3\phi + D \cos 3\phi$
Trigonal	32, 3m,	D
	3m	שכ 205 ע
	6, <del>6</del> ,	٨
Hexagona <b>l</b> .	6/m	A
	622, 6mm,	0
	6m2, 6/mam	U

The Quantity  $\overline{\Phi} = e_{2i}(o_jh_k^e + e_{1j}h_k^o)^P \times_{ijk}^{EH}$ 

$$A = S_{2} \left[ (1 - C_{1}C)(311) - S_{1}S(333) \right] - C_{2} \left[ S_{1}C(113) + C_{1}S(131) \right]$$
  

$$B = -C_{2}(1 + C_{1}C)(222)$$
  

$$D = C_{2}(1 + C_{1}C)(111)$$
  

$$P_{X_{ijk}^{Eh}} = (ijk)$$
  

$$S_{2} = \sin(\theta + \alpha_{2}), S_{1} = \sin(\theta + \alpha_{1}), S = \sin\theta$$
  

$$C_{2} = \cos(\theta + \alpha_{2}), C_{1} = \cos(\theta + \alpha_{1}), C = \cos\theta$$

### Table A-XVI

The Quantity  $\overline{\Phi} = e_{2i}n_j \epsilon^{ijk} (o_l e_{lm} + e_{ll}o_m)^M \chi_{mlk}^{EE}$ 

Crystal Class	Point Group	$\Phi$		
	4, 4, 4/m	A		
Tetragonal	422, Lmm, 42m, 4/mmm	0		
	3, 3	$A + B \cos 3\phi + D \sin 3\phi$		
Trigonal	32, 3m, Īm	B cos 3Ø		
	6, <b>ē</b> , 6/m	A		
Hexagonal	622, 6mm, 6m2, 6/mmm	Ο		

$$A = -S_{1} [(131) + (311)] \cos \alpha_{2}$$
  

$$B = -2C_{1}(111) \cos \alpha_{2}$$
  

$$D = -2C_{1}(222) \cos \alpha_{2}$$
  

$$M \chi_{mlk}^{EE} = (mlk)$$
  

$$S_{1} = \sin (\theta + \alpha_{1}), C_{1} = \cos (\theta + \alpha_{1})$$

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