

ORGANIC ELECTRO-OPTIC MATERIALS

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by

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Dedicated to my parents -

Caradog and Catherine Owen

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ABSTRACT

The basic theory of the electro-optic effect is explained and some current theories of non-linear optical effects are reviewed. Some guidelines on which potential electro-optic materials were selected are given. Preliminary tests included piezoelectric, pyroelectric and second harmonic generation tests on sixty organic compounds, nineteen of which gave positive results. Results of space group determinations are reported for 2-methyl 3-nitroaniline, 4-nitrophenylhydrazine and N-formyl 4-nitrophenylhydrazine (FNPH).

The theories of crystal growth are applied to the solution growth of FNPH. Various techniques applied for solution growth of this compound are described, one of which gave a crystal large enough for electro-optic evaluation.

Results are given of refractive index determinations, electro-optic half-wave voltages, both at d.c. and high frequency, of FNPH. The infrared and ultraviolet spectra of the compound are illustrated.

The results are discussed with respect to a proposed crystal structure then the device applications are considered. Possible uses of FNPH are suggested by a S.H.G. efficiency as high as metanitroaniline, by an electro-optic half-wave voltage of 12 kv.

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CHAPTER 1 - INTRODUCTION

1.1. Linear Optics

The most important property of an optical material is probably its refractive index, n . Its simplest definition arises from the observation that the velocity of light, v , in a dielectric medium differs from the vacuum value - the universal constant c ,

$$n = \frac{c}{v} \quad (1.1)$$

An electrical derivation of the refractive index is given by a manipulation of Maxwell's equations giving the results,

$$\begin{aligned} \nabla^2 E &= \epsilon \mu \frac{d^2 E}{dt^2} \\ \nabla^2 H &= \epsilon \mu \frac{d^2 H}{dt^2} \end{aligned} \quad (1.2)$$

where ϵ = permittivity of the material

μ = permeability of the material

which shows that electromagnetic waves may traverse the medium with a velocity $(\epsilon \mu)^{-1/2}$

In free space, $\epsilon = \epsilon_0$

$\mu = \mu_0$

and $(\epsilon_0 \mu_0)^{-1/2} = c$

In a non-magnetic material,

$\epsilon = K \epsilon_0$

$\mu = \mu_0$

where K = relative susceptibility (dielectric constant)

Hence the velocity of light in the material is reduced from c by a factor,

$$n = \sqrt{K} \quad (1.3)$$

The dielectric constant, K , may differ greatly from its d.c. value at optical frequencies and, together with n , is subject to dispersion by the optical absorption bands which are distributed throughout the spectrum of the dielectric material. For each band, maximum absorption occurs when the incident light has the frequency of a natural resonance of bound charges in the material. At such a frequency the medium is seen as a collection of real or imaginary oscillators, e.g. polar bond vibrations causing infrared absorption or electronic transitions leading to absorption of ultraviolet light.

The following analysis due to Lorentz (Longhurst (1957)), written in simplified form, shows how the refractive index is related to the oscillating charges. The nature of each oscillator is not specified, but each is defined by its resonant frequency ω_0 , and its oscillator strength f , the number of "unit oscillators" per molecule. The reaction of the medium to an electromagnetic wave $E = E_0 e^{i\omega t}$ is written:

$$P = z \epsilon_0 E \quad (1.4)$$

where P = polarization

z = electric susceptibility

$$\text{and } P = N_0 e f x \quad (1.5)$$

where N_0 = molecular density

e = electronic charge

x = coordinate representing charge distribution.

A single electronic oscillator is defined:

$$\ddot{x} + \omega_o^2 x = \alpha \frac{e}{m} E \quad (1.6)^*$$

m = electronic mass

αE is the internal field

from (1.4)

$$\begin{aligned} \ddot{P} + \omega_o^2 P &= z \epsilon_o (\ddot{E} + \omega_o^2 E) \\ &= z \epsilon_o (\omega_o^2 - \omega^2) E \end{aligned}$$

from (1.5) and (1.6)

$$\ddot{P} + \omega_o^2 P = \frac{N_o f e^2 \alpha E}{m}$$

$$\text{then } z = \frac{N_o f e^2 \alpha}{\epsilon_o m (\omega_o^2 - \omega^2)}$$

for a single, one dimensional, absorption band model.

In the three-dimensional case, we have

$$z = \frac{3 N_o f e^2 \alpha}{\epsilon_o m (\omega_o^2 - \omega^2)}$$

A refinement of this formula can be made by estimating a value of α . In the case of cubic symmetry we have (Kip (1962)),

$$E_{loc} = E + \frac{P}{3\epsilon_o}$$

$$\text{then } \alpha = 1 + \frac{z}{3}$$

*The effect of damping has been omitted for simplicity.

Substitution of this value of α gives

$$\frac{z}{z+3} = \frac{N_o f e^2}{\epsilon_o m (\omega_o^2 - \omega^2)}$$

Since $z = K + 1$ and $K = n^2$, we have the Lorenz-Lorentz formula for the refractivity,

$$R = \frac{n^2 - 1}{n^2 + 2} = \frac{N_o f e^2}{\epsilon_o m (\omega_o^2 - \omega^2)} \quad (1.7)$$

The approximations do not hold near $\omega = \omega_o$, but either side of the absorption peak the formula successfully predicts the familiar Sellmeier dispersion (Fig. 1.1). At frequencies remote from ω_o , the absorption band has no dispersive influence. Therefore we may formulate the refractivity as a constant "background level" from oscillators at various frequencies with a perturbation due to an oscillator with a frequency close to that of the incident light:

$$\frac{n^2 - 1}{n^2 + 2} = A + B \frac{f}{\omega_o^2 - \omega^2} \quad (1.8)$$

From this equation we note that a change of f or ω_o will result in a change in refractive index.

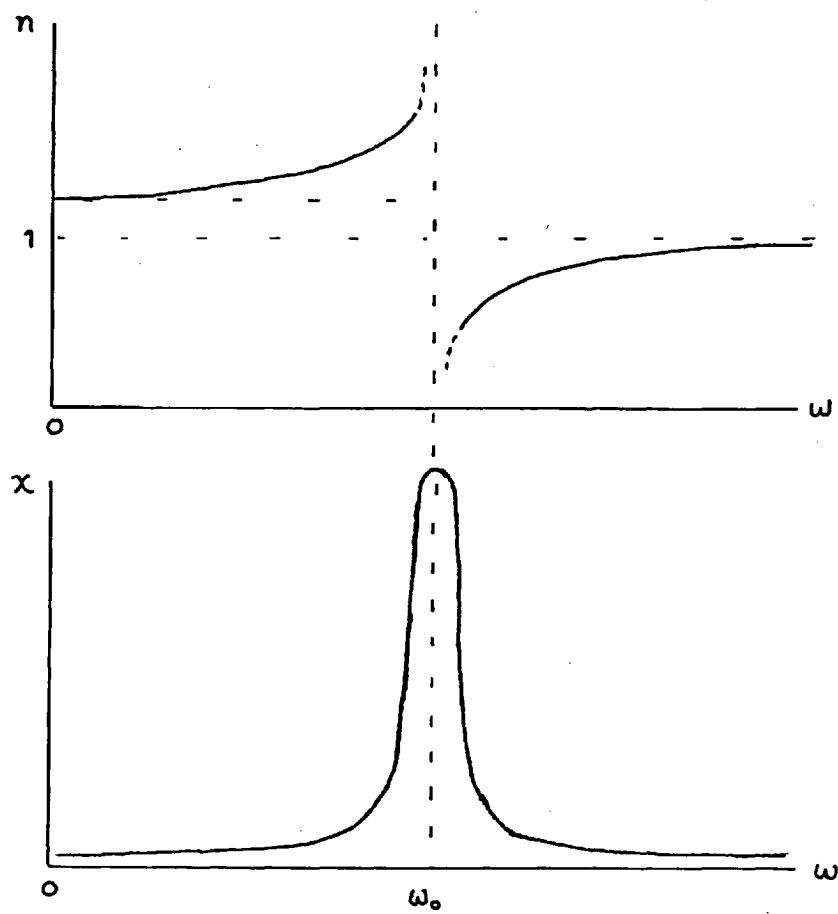
1.2. Non-linear Optics

The term "non-linear optics" is misleading if it suggests that light does not travel in straight lines! The implication should be that the polarization of a medium varies non-linearly with field,

$$\frac{P}{\epsilon_o} = X_L^L E + X_{(2)}^{NL} E^2 + X_{(3)}^{NL} E^3$$

where X_L^L = linear susceptibility = z

X^{NL} = non-linear susceptibility.



n = refractive index
 χ = extinction coefficient
 ω = wavelength

Fig. 1.1 - Sellmeier dispersion of the refractive index.

Considering the structure of matter, this must be the case. An ion moving from its equilibrium position eventually encounters forces of an entirely different nature to those represented by a simple potential well; similarly a covalent bond can only be stretched to its breaking point. Therefore, in any real case there are small deviations from linearity near the equilibrium position and these escalate at large displacements.

Fig. 1.2 shows how a second-order non-linearity of P leads to an anharmonic potential well. The consequence of the non-linearity is that the elastic force constant of a vibrating charge, which determines ω_0 , is dependent on the applied field. A resultant shift in ω_0 with applied field has been calculated as (Kurtz and Robinson (1967)):

$$(\omega'_0)^2 = \omega_0^2 + \frac{2 v e \beta E(0)}{m \omega_0^2} \quad (1.9)$$

v = anharmonicity constant

$$\Delta \omega_0 = \frac{2 v e}{m \omega_0^3} \beta E(0) \quad (1.10)$$

$\beta E(0)$ = internal field.

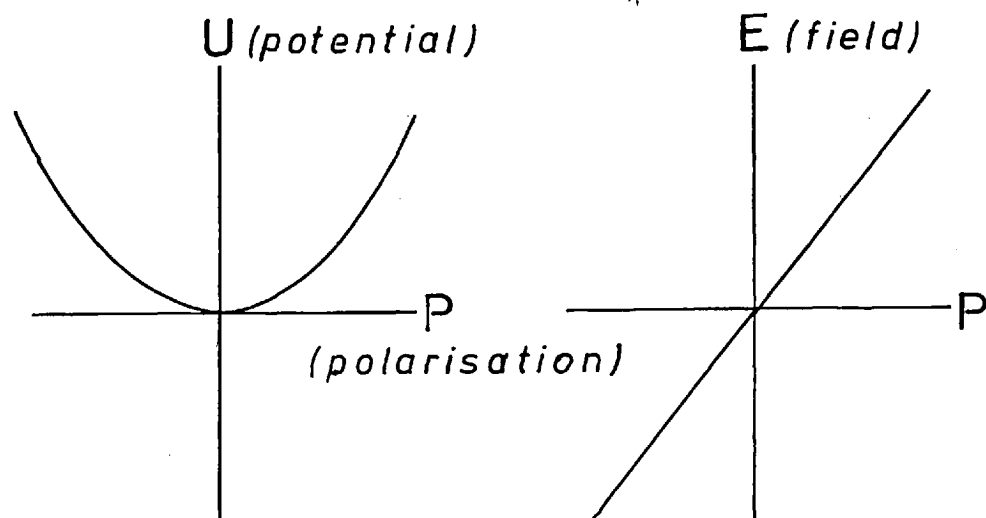
If the "oscillator" is described as an electronic transition, a similar result follows from energetic considerations:

$$\Delta \mathcal{E} = \beta' E(0) \Delta \mu \quad (1.11)$$

where, $\mathcal{E}$ is the transition energy

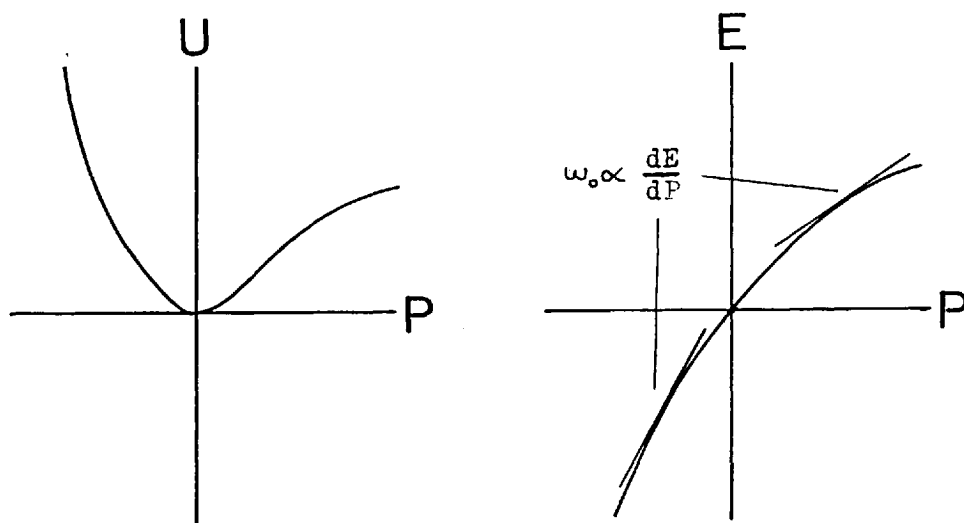
$\beta' E(0)$ is the internal field

$\Delta \mu$ is the dipole moment change incurred during transition.



linear polarization, $\frac{dE}{dP} = \text{constant}$

Harmonic Potential



non-linear polarization, $\frac{dE}{dP} = f(E)$

Anharmonic Potential

Fig.1.2 - The equivalence of anharmonic potential to non-linear polarization in a dielectric.

$$\Delta \omega_0 = \beta' E(0) \frac{\Delta \mu}{\hbar} \quad (1.12)$$

Direct evidence of a linear shift in ω_0 with applied field has been found in the organic solid metanitroaniline; the phenomenon was called the linear electro-chromic effect (Stevenson et al (1973)). (Any confusion of terms is checked here: the linear electro-chromic effect is so called because of the direct proportionality between ω_0 and E ; however, since it derives from a non-linear polarization, it is included in the group of non-linear optical effects.)

Bearing in mind the Sellmeier dispersion mentioned above, it is clear that a perturbation of the absorption band structure causes a corresponding change in refractive index. Thus we have another effect of a non-linear polarization, the electro-optic effect. A further important effect within this group is second harmonic generation (S.H.G.), which follows directly from the radiation field of a charge vibrating in the anharmonic potential well of Fig. 1.2. To describe these and other non-linear optical properties a notation was devised by Bloembergen (1965) in which two applied fields, $E \exp i\beta t$ and $E \exp i\gamma t$ produce a polarization at the sum frequency $\alpha = \beta + \gamma$;

$$\frac{P_i}{\epsilon_0} \exp i\alpha t = d_{ijk}^{\alpha\beta\gamma} E_j^\beta E_k^\gamma \exp i(\beta + \gamma) t \quad (1.13)$$

where $d_{ijk}^{\alpha\beta\gamma}$ is the second order non-linear susceptibility tensor.

Letting $\beta = \omega$, $\gamma = 0$ we have the non-linear susceptibility $d_{ijk}^{\omega,\omega,0}$. This generates a polarization at frequency ω , which is added to the linear polarization which determines the refractive index.

Thus we have an electro-optic effect. $\beta = \omega$, $\gamma = \omega$ yields a non-linear

polarization at frequency 2ω which represents S.H.G.

A non-zero value of $d_{ijk}^{\alpha\beta\gamma}$ only arises if there is a second order non-linearity of the potential well containing the relevant vibrator.

This cannot occur if the crystal structure is centrosymmetric. Thus the behaviour of the tensor $d_{ijk}^{\alpha\beta\gamma}$ is analogous to that of the piezoelectric tensor in that it becomes zero under the inversion operation:

$$\begin{aligned} \text{If } d_{ijk} &= d_{(-i)jk} \\ &= -d_{ijk} \end{aligned}$$

$$\text{then } d_{ijk} \equiv 0.$$

The electro-optic effect and S.H.G. are now discussed in greater detail.

1.3. The Electro-optic Effect

1.3.1. Crystal optics

In the first section, the origin of the refractive index was traced to the dielectric susceptibility inherent in the bound charges within the medium. The discussion was limited to oscillators vibrating in one dimension only. The argument is similar in the three dimensional case, except that each oscillator must be described by a tensor, and the oscillator strength tensor is obtained by summation over the unit cell of the material. The susceptibility tensor must obey Neumann's principle (Nye(1957)), i.e. it is symmetric and obeys the symmetry of the crystal class. Thus optical materials are classified in three groups:

- (1) Isotropic - This group includes glasses and solids of the cubic class, which have constant optical properties irrespective of direction. If an optical property be represented by a vector whose length is proportional to the magnitude of the property, and whose direction is

the direction of the light polarization, the locus of the vector will describe a sphere.

(2) Uniaxial - Crystals of the trigonal, tetragonal and hexagonal classes have rotational symmetry of optical properties about the axis of symmetry, so that the "property vector" here describes an ellipsoid of revolution. The crystals are potentially dichroic, i.e. they have two independent absorption bands for axial and radial polarisation directions.

(3) Biaxial - The remaining classes are orthorhombic, monoclinic and triclinic. The vector here describes a general ellipsoid; there may be three independent absorption bands and the material is pleochroic.

A strong dichroism or pleochroism, shown by marked absorption of light when polarised along a particular direction in the crystal, indicates that the resonant transitions or oscillators are closely aligned with that direction. An example is the polarizing filter in which a light-absorbing polymer has been stretched to align the molecules so that their transition moments lie parallel.

1.3.2. Birefringence

To include cases of electrical anisotropy, the dielectric constant should be generally represented by a tensor:

$$D_i = \epsilon_o K_{ij} E_j \quad (1.14)$$

The equation shows that the electric displacement D and the electric field E have in general different directions. From this it follows that the ray direction, i.e. the path of energy flow, given by E x H (H is the magnetic field) need not be coincident with the wave-normal, D x H. A solution of Maxwell's equations for this case shows that for a given wave-normal, only two polarization directions

are allowed (Longhurst (1957)). These two vibration directions are orthogonal and any other polarization state is resolved between them. The refractive indices for the two polarization directions will not be equal and are determined from the refractive index ellipsoid, called Fletcher's Indicatrix (Fig. 1.3). The three principal axes of this general ellipsoid represent the three principal indices of refraction. For a given wave normal, the major section of the ellipsoid perpendicular to the wave normal is an ellipse, whose major and minor axes represent the allowed polarization directions, and the corresponding refractive indices. Under increasing symmetry, the ellipsoid degenerates through an ellipsoid of revolution to a sphere. (The terms uniaxial and biaxial refer to optic axes - normal to the unique circular sections of the ellipsoid in which refractive index is independent of direction. There are two such axes in the general ellipsoid but only one in an ellipsoid of revolution.)

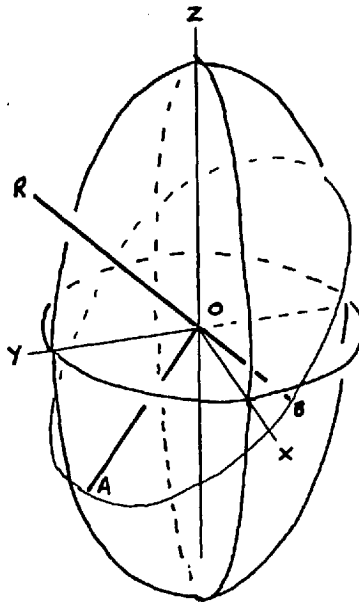
The indicatrix may be defined in terms of its principal axes x'_1, x'_2, x'_3

$$\frac{x'^2_1}{n_1^2} + \frac{x'^2_2}{n_2^2} + \frac{x'^2_3}{n_3^2} = 1 \quad (1.15)$$

where n_i = principal indices

$i = 1, 2, 3$

The lengths of the semi-axes of the ellipsoid are numerically equal to the principal refractive indices. The axes x'_i will not, in general, coincide with the crystallographic axes x_i . To represent the indicatrix in terms of the latter, the tensor notation is used:



$OX, OY, OZ,$ = Principal index directions

OR = Wave normal

$OA, OB,$ = Privileged directions

Fig.1.3 - Fletcher's indicatrix.

$$B_{ij} x_i x_j = 1 \quad (1.16)$$

$$\text{where } B = \frac{1}{n^2}$$

B_{ij} may be written in matrix form:

$$\begin{pmatrix} B_{11} & B_{12} & B_{13} \\ B_{21} & B_{22} & B_{23} \\ B_{31} & B_{32} & B_{33} \end{pmatrix}$$

which, since $B_{ij} = B_{ji}$ by symmetry may be condensed to B_i :

$$(B_1, B_2, B_3, B_4, B_5, B_6) \quad \text{where } B_4 = B_{23}$$

$$B_5 = B_{13}$$

$$B_6 = B_{12}$$

The last three coefficients will be zero if the indicatrix axes coincide with the crystallographic axes; non-zero values indicate a rotation of the ellipsoid from the crystallographic axes and therefore the coefficients B_4 , B_5 and B_6 are called skew coefficients.

1.3.3. The electro-optic tensor

The electro-optic effect outlined in sec. 1.2 is now seen as a field perturbation of the indicatrix:

$$\frac{dB_i}{dE_j} = r_{ij} \quad (1.17)$$

$$i = 1, 2, \dots, 6$$

$$j = 1, 2, 3$$

r_{ij} is a tensor of the third rank like d_{ijk} and the piezoelectric tensor. For the point group mm2 the tensor may be written:

$$\begin{pmatrix} \cdot & \cdot & \cdot & \cdot & r_{51} & \cdot \\ \cdot & \cdot & \cdot & r_{42} & \cdot & \cdot \\ r_{13} & r_{23} & r_{33} & \cdot & \cdot & \cdot \end{pmatrix}$$

The blank positions indicate components identical to zero by symmetry. The remaining principal axes components r_{13} , r_{23} and r_{33} represent increases in β , hence decreases in n for light polarized along directions X, Y or Z respectively on application of an electric field along Z. The skew components represent rotations of the ellipsoid about axes Y and Z on application of fields along Y and Z respectively.

1.3.4. Half-wave voltage

Observed changes in refractive index on application of a field are extremely small and are measured in terms of the phase change at the end of a given light path through the medium. Thus an electro-optical retardation, Γ_e , is defined:

$$\Gamma_e = + \frac{2\pi\ell}{\lambda_0} (n' - n) \quad (1.18)$$

ℓ = light path

λ = wavelength in vacuo

n' = refractive index under the
influence of the field.

For the coefficient r_{13} ,

$$dB_1 = r_{13} \cdot E_3$$

$$dn_1 = -\frac{n_1^3}{2} dB_1 = -\frac{n_1^3}{2} r_{13} \cdot E_3$$

For light polarized along X,

$$\Gamma_e^x = -\frac{\pi \ell}{\lambda_0} n_1^3 r_{13} E_3$$

and $\frac{d\Gamma_e^x}{dE_3} = -\frac{\pi \ell}{\lambda_0} n_1^3 r_{13}$ (1.19)

The half-wave voltage, $V'_{\lambda/2}$, is defined as the voltage across parallel electrodes required to introduce a retardation $\Gamma_e = \pi$ into

$$\text{the light path so that } V'_{\lambda/2} = \frac{d}{\ell} \frac{\lambda_0}{n_1^3 r_{13}} \quad (1.20)$$

where d = interelectrode spacing.

The above definition applies to an electro-optic device of specified aspect ratio $\frac{d}{\ell}$. A normalized half-wave voltage is used to characterize a material:

$$V_{\lambda/2} = -\frac{\lambda_0}{n_1^3 r_{13}} \quad (1.21)$$

The half-wave voltage corresponding to r_{13} would be measured interferometrically by passing a beam polarized along X through the crystal and superimposing on it a coherent reference beam. Destructive and constructive interference would occur at half-wave intervals as the field was altered.

An easier demonstration of electro-optic retardation may be achieved by an exploitation of the crystal's natural birefringence. An input beam polarized at 45° to the vibration directions will be resolved into orthogonally polarized components. The two beams,

subject to different refractive indices will emerge with a phase difference, or optical retardation, Γ_o .

e.g. for a wave polarised at 45° from X towards Y,

$$\Gamma_o^{Y-X} = \frac{2\pi\ell}{\lambda_o} (n_2 - n_1) \quad (1.22)$$

Unlike the previous case, this phase difference can be measured without a reference beam. Depending on the retardation, the two waves combine on emerging to give various states of polarization identifiable with an analyzing filter crossed with respect to the initial polarizer. The sign of the retardation is ambiguous but may be determined by interpolation of a standard quartz wedge between crystal and analyzer (Fig. 1.4).

On application of a field, the phase difference will be subject to an additional electro-optic retardation:

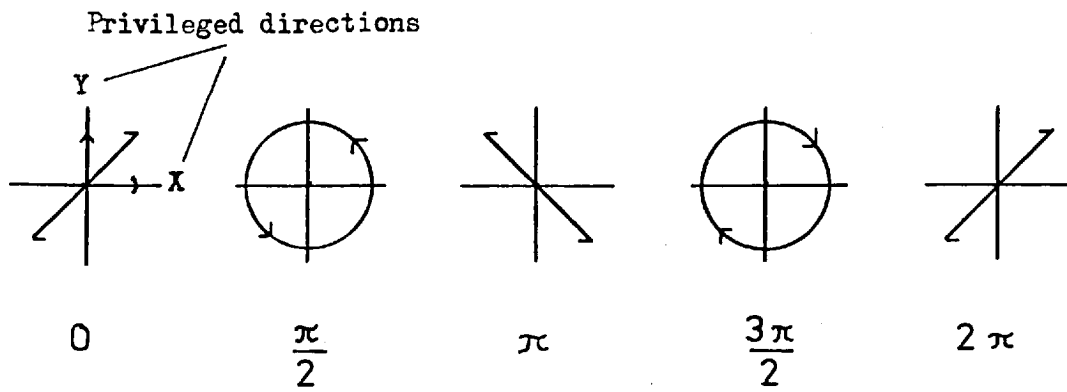
$$\begin{aligned} \Gamma^{Y-X} &= \Gamma_o^{Y-X} + \Gamma_e^{Y-X} \\ &= \Gamma_o + \frac{2\pi\ell}{\lambda_o} [\Delta n_2 - \Delta n_1] E \end{aligned} \quad (1.23)$$

with a half-wave voltage:

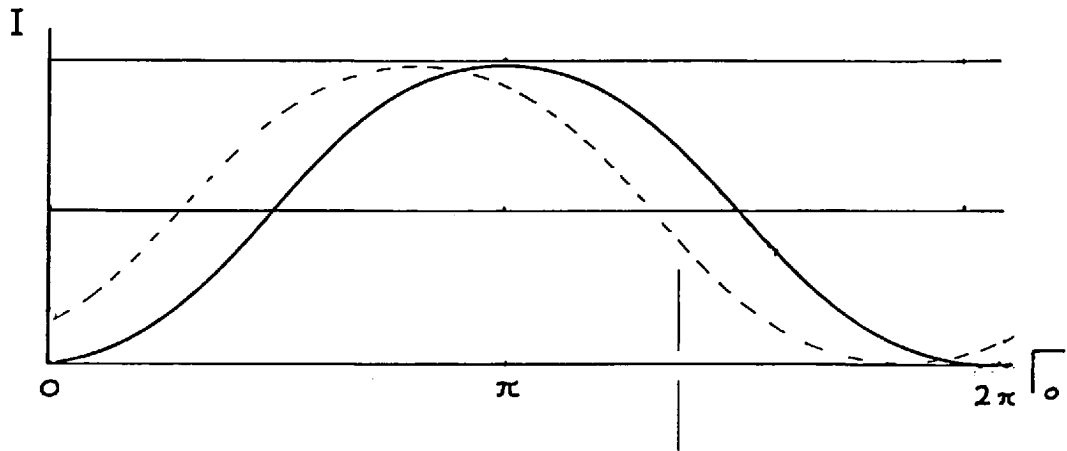
$$V_{\lambda/2}^{Y-X} = - \frac{\lambda_o}{n_2^3 r_{23} - n_1^3 r_{13}} \quad (1.24)$$

1.3.5. Electro-optic modulation

Referring to Fig.1.4 we see that the light output from the arrangement of polarizer, crystal, quartz wedge and analyzer varies as:



(a) Polarization direction versus optical retardation



Effect of increasing quartz wedge thickness

(b) Transmission through an analyzing filter

Fig.1.4 - Optical retardation in a birefringent crystal plate.

$$I = \frac{1}{2} I_0 (1 - \cos \Gamma) \quad (1.25)$$

If the quartz wedge is adjusted so that for the whole system $\Gamma_0 = \frac{\pi}{2}$, I varies almost linearly with Γ_e over a limited region:

$$\begin{aligned} I &= \frac{1}{2} I_0 [1 - \cos (\frac{\pi}{2} + \Gamma_e)] \\ &= \frac{1}{2} I_0 [1 + \sin \Gamma_e] \approx \frac{1}{2} I_0 (1 + \Gamma_e) \end{aligned}$$

If $E = E_0 \sin \omega t$, $\Gamma_e = kE$ where $k = \frac{\pi \ell}{\lambda_0} (n_2^3 r_{23} - n_1^3 r_{13})$

$$I = \frac{1}{2} I_0 (1 + kE_0 \sin \omega t) \quad (1.26)$$

This represents an output beam modulated at the frequency of the applied field with modulation depth $\frac{1}{2} kE_0$.

Another case arises when $\Gamma_0 = 0$,

$$\begin{aligned} I &= \frac{1}{2} I_0 (1 - \cos \Gamma_e) \approx \frac{1}{4} I_0 \Gamma_e^2 \\ &= \frac{1}{4} I_0 k^2 E^2 \sin^2 \omega t \\ &= \frac{1}{8} I_0 k^2 E_0^2 (1 - \cos 2\omega t) \end{aligned} \quad (1.27)$$

This represents modulation at twice the frequency of the applied field with modulation depth $\frac{1}{8} k^2 E_0^2$.

The first case is practically useful and therefore a modulator should incorporate an electrical or optical bias so that maximum modulation can be achieved with minimum distortion.

1.4. Second Harmonic Generation

Although S.H.G. was not of primary importance in this work, the effect is briefly mentioned here as it was the major tool used for the discovery of non-linear materials.

S.H.G. is one of a host of non-linear optical effects predicted by the general theory of non linear polarization illustrated by eqn. (1.13). In this case we have,

$$P_i^{2\omega} = d_{ijk}^{2\omega, \omega, \omega} E_j E_k \exp 2 i \omega t$$

Since the formula is quadratic in E , the field intensity of the incident beam, intense light sources must be used to detect S.H.G.; the second harmonic would be expected to become dominant only when the optical field approached the binding field on the dispersion electron, typically 10^8 V M^{-1} . Hence powerful laser sources must be used which can attain field strengths up to about 10^6 V M^{-1} . Under favourable conditions the effect may be observed as a partial conversion of an incident infra-red beam from a Nd:YAG laser ($\lambda = 1.06 \mu$) into visible green light (0.53μ).

The tensor d_{ijk} indicates the polarization direction of the second harmonic beam generated by a given input beam, but the wave-front and ray directions are not so simply determined. Because of the difference in refractive index between the fundamental and its second harmonic, the latter will generally be greatly attenuated by destructive interference. However, it is possible, in the case of birefringent crystals, to find special directions in which the two indices are equal. If the input beam is suitably directed, phase matching occurs between the two beams and second harmonic conversion becomes much more efficient (Maker et al (1962)). Deliberate phase

matching was outside the scope of this project but as an alternative, S.H.G. experiments were performed on powder specimens, in which various crystal orientations were offered to the input beam so that at least some crystals could efficiently generate the harmonic. Because the samples compared varied widely in geometrical form and refractive properties, the intensity of second harmonic generated by a sample was not taken to be representative of the value of d_{ijk} . However, the generation of second harmonic by a material was taken as a verification of a non-zero value of d_{ijk} and hence the material could be assigned to a non-centrosymmetric point group.

1.5. Electro-optic materials

The basic requirements of an electro optic material are (e.g. Kaminow and Turner 1966):

- 1) Availability of large single crystal form.
- 2) Optical homogeneity of the crystal.
- 3) Chemical stability.
- 4) Mechanical stability sufficient to allow fabrication of oriented, cut and optically polished bars of the required size.
- 5) A high resistivity.
- 6) A low half-wave voltage.
- 7) A low refractive index which facilitates matching of optical components.

If these requirements are met, the material may be of use in electro-optic devices, e.g. laser Q-switches, beam deflectors and beam intensity modulators. This work concerns the latter application for which the dielectric loss and control energy must be low at frequencies up to the GHz range. A figure of merit is $K V_{\lambda/2}^2$ (Denton et al (1967)), which is proportional to the control energy.

An attractive feature of organic electro-optic materials is the purely electronic mechanism of the electro-optic effect. Some of the current inorganic materials, tabulated in Table 1.1, receive significant contributions to their electro-optic effects from highly polarizable anions (Garrett (1968)) and are therefore prone to having anomalously large dielectric constants and high dielectric losses at high frequencies. Potassium Dihydrogen Phosphate (KDP) and its isomorphs are currently used in electro-optic modulators but all members of the group have piezo-electric resonances near 100 MHz, which prohibit their use for modulation at such frequencies.

Some materials of the ferroelectric group, however, have half-wave voltages low enough to offset their undesirably large dielectric constants: examples of these are Barium Sodium Niobate ($\text{Ba}_2\text{NaNb}_5\text{O}_{15}$) and Strontium Barium Niobate ($\text{Sr}_3\text{BaNb}_8\text{O}_{24}$). However, there is a formidable problem concerning the growth of electro-optically homogeneous crystals of these materials. The relative concentrations of three metals and oxygen must be kept constant during growth if refractive index variations are to be avoided; this is extremely difficult because the vapour pressures of the four constituents are different and evaporation of the melt continually upsets the delicate concentration balance needed for the growth of the required composition. Furthermore, the respective segregation coefficients are dependent on hydrodynamic conditions which inevitably fluctuate during growth.

Organic crystals, however, are grown relatively easily and cheaply by low temperature methods, which require no control on composition (apart from purity) since only one constituent is present. The crystals produced are relatively free from the strain observed in materials grown at high temperatures for two reasons: the difference between growth temperature and room temperature is smaller and therefore a

slower cooling programme may be used; also the crystals are softer and strain annealing may take place more easily.

Albeit a naive approach to a theoretician, the analysis of Sec. 1.2, particularly eqn. (1.12) suggests that large electro-chromic, and hence electro-optic, effects may occur where the molecule has an electronic transition involving a large change in dipole moment. For that reason this work is directed at compounds consisting of an aromatic ring substituted with both electron donating and electron accepting groups together. One compound of this type, MNA, has been characterised electro-optically and has been found to have a favourably low value of $K V_{\lambda/2}^2$ (Stevenson (1973)).

A transition with a large dipole moment change thus may form a basic prerequisite for a large electro-optic effect in an organic material. However, since the effective field of the light wave at a visible wavelength is macroscopic relative to the individual molecules, it is the average dipole moment change, i.e. the tensor summation of the molecular oscillator strengths, that will determine the intensity of the electro-optic effect. Cancellation will be diminished if the lattice is highly asymmetric with respect to the transition moment direction. Such asymmetry may be detected, and to a lesser degree quantified by an observation of some other non-linear properties of the material such as piezoelectricity, pyroelectricity or S.H.G.

The contribution of the above factors toward non-linear effects is illustrated by an empirical rule by Miller (1964), which was later treated theoretically by Garrett and Robinson (1966).

$$d_{ijk}^{\alpha\beta\gamma} = \Delta_{ijk} \chi_{ii}^{\alpha} \chi_{jj}^{\beta} \chi_{kk}^{\gamma} \quad (1.28)$$

where $d_{ijk}^{\alpha\beta\gamma}$ is the non-linear susceptibility

χ_{ii} are the linear susceptibilities

Here the non-linear susceptibility is broken down into the linear susceptibilities, which determine the dispersion effects, and Δ_{ijk} which is almost independent of frequency for a given material. Δ_{ijk} is clearly some indication of the asymmetry of the lattice. The variation in Δ for different materials (Table 1.1) spans only two orders of magnitude - from 0.2×10^{-6} esu to 20×10^{-6} esu (Robinson (1967)) - a variation comparable to the range expected statistically from different degrees of asymmetry. The theoretical work of Robinson derives a proportionality between Δ_{ijk} and t_{ijk} , the cubic moment of the ground state electronic distribution. The latter, although of fundamental importance in defining asymmetry, has little practical significance at present because of the lack of experimentally determined values.

The aim of this project was to investigate a small field of organic compounds with the ultimate objective of characterising potentially useful electro-optic materials. The theory presented in this introductory chapter is an oversimplification of the real situation which is more correctly described by a quantum mechanical treatment. The complexity of the latter, however, proved to be prohibitive, and the simple theory justified itself by providing a path into the uncultivated jungle of organic chemistry.

Table 1.1

Compound	Type	mk	r_{mk}^T ($\times 10^{-12} \text{mV}^{-1}$)	K	$V_{\lambda/2}$ (KV)	$KV_{\lambda/2}^2$	$\lambda(\text{nm})$
ADP	non-polar	63	8.55	15	10	1,500	632.8
KDP	non-polar	63	10	20	9.6	1,800	633.0
KD*P	non-polar	63	20-26	50	3	450	546.0
LiNbO_3	ferroelectric	33	32	30	3	270	632.8
1) $\text{Sr}_{0.75}\text{Ba}_{0.25}\text{Nb}_2\text{O}_6$	ferroelectric	33	1340	3400	0.048	8	632.8
2) MNA	polar, organic	33	16.7	4.6	8.5	300	632.8

1) Lenzo (1967)

2) Stevenson (1973)

other data from Milek (1972)

CHAPTER 2 - PRELIMINARY INVESTIGATION

Although some organic electro-optic materials (e.g. HMTA, MNA) had been discovered before the start of this project, these were not members of groups of isomorphous compounds such as are encountered in the inorganics. Therefore a logical programme of substitution of isoelectronic atoms or groups as commonly adopted in inorganic research did not apply here. A more productive approach was a preliminary investigation of a large number of compounds with respect to the condition of asymmetry described in Chapter 1.

Unlike inorganic compounds, whose crystal structures are well documented and to some extent predictable, organic compounds have received no such systematic study because in organic chemistry the emphasis lies on molecular rather than crystallographic structure. The relatively weak intermolecular bonding and the numerous possible molecular conformations of organic solids make structural predictions very difficult. In the search for non-centrosymmetric organic solids, a literature survey produced only isolated cases of obscure compounds which were often difficult to obtain. A practical investigation of readily available compounds was therefore much more useful and comprised:

- (1) Selection of compounds, preferably highly coloured, in which intramolecular charge transfer transitions were likely.
- (2) Purification of each compound.
- (3) Testing for non-centrosymmetric properties.
- (4) Feasibility studies of crystal growth.
- (5) Crystallographic studies on non-centrosymmetric crystals.

The selected compounds are shown in Table 2.1. Many of these are simply substituted nitroanilines whose spectral properties were expected to resemble MNA, which is known to have an electro-optically

3-nitroaniline (Z)	2-nitrophenylhydrazine (E)
2-methyl 3-nitroaniline (S)	4-nitrophenylhydrazine (E)
2-methyl 5-nitroaniline (Z)	N-formyl 4 nitrophenylhydrazine (E)*
3-methyl 6-nitroaniline (Z)	2,4-dinitrophenylhydrazine (E)
4-methyl 3-nitroaniline (Z)	4-nitrophenylhydrazones*
3-methyl 4-nitroaniline (Z)	and
4-methyl 2-nitroaniline (Z)	2,4-dinitrophenylhydrazones* of
2-amino 3-nitroaniline (Z)	Formaldehyde, Acetone, Acetaldehyde
4-amino 3-nitroaniline (S)	Benzaldehyde, Acetophenone, Benzo-
3-amino 4-nitroaniline (S)	phenone (E) (A) (EA)
4-nitro 3-trifluoroaniline (S)	azobenzene (B)
4-nitro 2-trifluoroaniline (Z)	4-hydroxyazobenzene (E)
2-nitro 5-trifluoroaniline (S)	4-amino azobenzene (E)
4-methoxy 3-nitroaniline (Z)	4-methoxyazobenzene (E)
3-methoxy 6-nitroaniline (Z)	phthalodinitrile (E)
4-methoxy 2-nitroaniline (Z)	benzil (Z)
2-methoxy 4-nitroaniline (Z)	1,4-naphthoquinone (Z)
3,5 dinitroaniline (S)	9-anthraldehyde (Z)
1,3 dinitrobenzene (Z)	acenaphthene picrate (A)*
2,3 aminonitripyridine (Z)	fluorene (B)
2,5 aminonitripyridine (Z)	anthracene (B)
N-methyl 4-nitroaniline (Z)	fluorescein (E)
2,4 dinitro N,N diethylaniline (S)	(Z) = zone refined
N,N-dimethyl nitroaniline (Z)	(S) = vacuum sublimed
2,4-dinitro 2' methoxydiphenylamine (Z)	(E) = crystallized from ethanol
2,4-dinitro 2' methyldiphenylamine (Z)	(A) = " " acetone
2,4-dinitro 3' methyldiphenylamine (Z)	(EA) = " " ethyl acetate
2-hydroxy 5-nitroaniline (A)	(B) = " " benzene
3-aminophenol (A)	
3-nitrophenol (A)	
4-nitrophenol (A)	

*compounds prepared in the laboratory.

Table 2.1. Materials tested in search for non-centrosymmetric structures.

active charge transfer band in the ultraviolet. The set was extended by inclusion of molecules with alternative groups to the amino and nitro groups which were responsible for the charge transfer in nitro-anilines. Compounds marked with an asterisk were prepared in the laboratory; others were obtained commercially.

The sixty compounds listed in Table 2.1 were purified then subjected to piezoelectric, pyroelectric and S.H.G. testing. Of the nineteen materials which registered a positive result, three were selected for crystallographic and crystal growth studies.

2.1. Purification Methods

2.1.1. Fractional Crystallization

This method of purification consists of dissolving the material to be purified in a chosen solvent then crystallizing some of the solute either by cooling or by partial evaporation of solvent. In theory, the solution would always be undersaturated with respect to impurities, provided their initial concentrations were low, and only the desired compound would separate. In practice, however, the ratio of the concentration of impurity in the solution to that in the crystal is finite, and repeated dissolution and crystallization, each time using fresh solvent, must be carried out to achieve a good separation. Each cycle in the process reduces the stock of material by an amount left in solution and wastage occurs; this is minimized by concentrating depleted solutions by solvent evaporation thus recovering solute which may be added to the starting material; a typical scheme is shown in Fig. 2.1.

2.1.2. Zone Refining

Crude starting material is loaded into a glass tube, melted, and resolidified to form a long cylinder of compact solid. A short zone

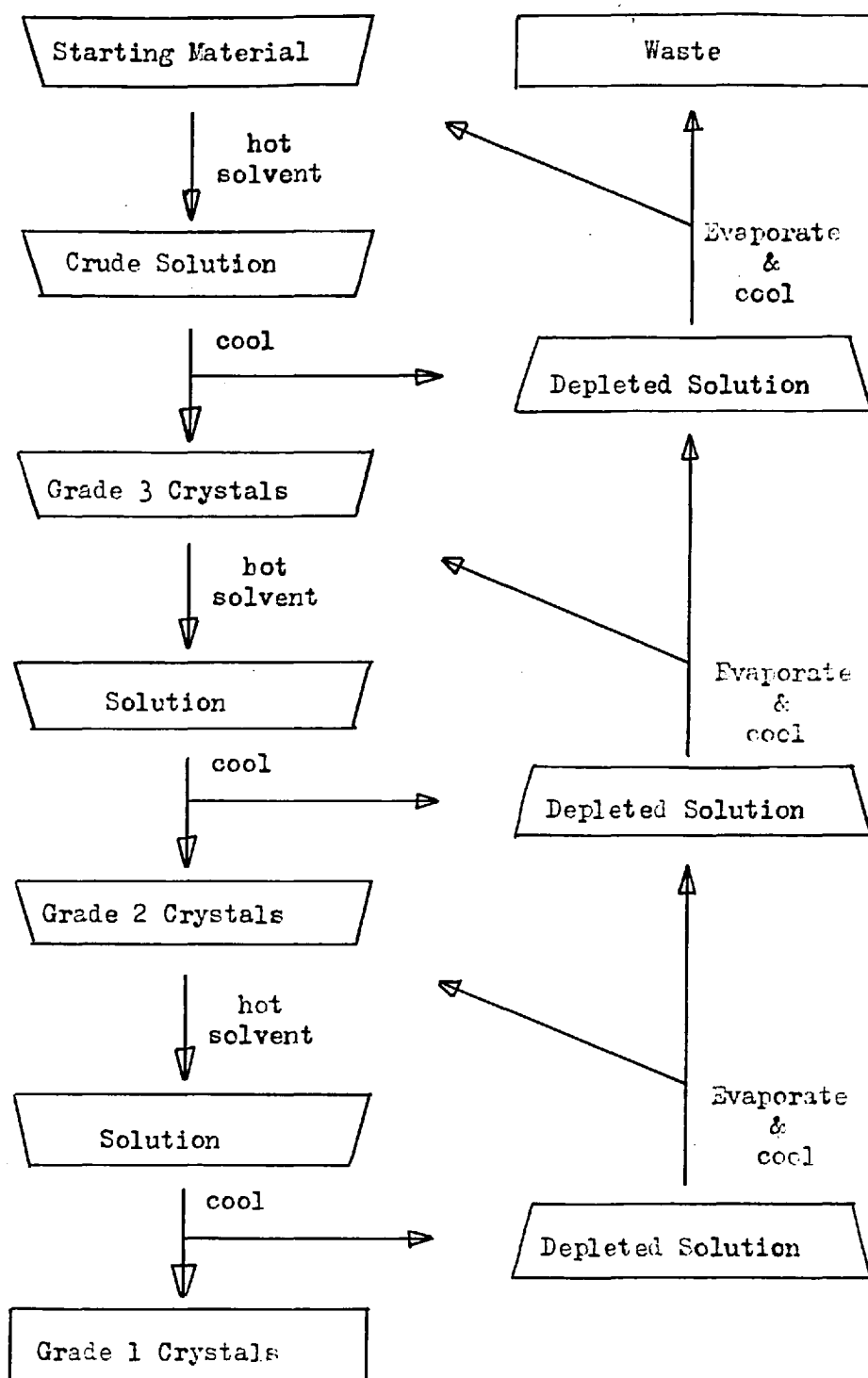


Fig 2.1 - Fractional Crystallization

is melted at the top of the cylinder and slowly moved, by moving the container relative to the heater, down the cylinder. This effects a continuous recrystallization behind the molten zone, which carries the impurities, solid and dissolved, down to the bottom of the tube. For any purification to take place the segregation coefficient of the impurity, i.e. the ratio of its concentration in the crystallizing solid to that in the liquid zone, must be less than unity. Each repetition of the process improves the purity of the solid in the upper part of the cylinder until the rate of purification is matched by an equal rate of thermal decomposition.

2.1.3. Vacuum Sublimation

A method of vacuum sublimation generally performed by chemists uses a liquid nitrogen cooled "cold finger" condenser to solidify vapour formed by gentle heating of the solid under vacuum. This method is rather indiscriminate, allowing impurities having vapour pressures similar to, or higher than, the desired compound to escape separation. A modified apparatus was used in this work and is shown in Fig. 2.2.

The thermal gradient along the substrate gave a crude separation of compounds with different vapour pressures. The flow of nitrogen facilitated vapour transport and also refined the separation by spreading out the condensed zone, in a manner analogous to column chromatography - components of the mixture with high vapour pressures were transported along the substrate at a greater rate than those with low vapour pressures.

2.2. Testing for Non-centrosymmetric Materials

Table 2.1 shows the purification method adopted for each compound. After purification, each compound was subjected to the three tests

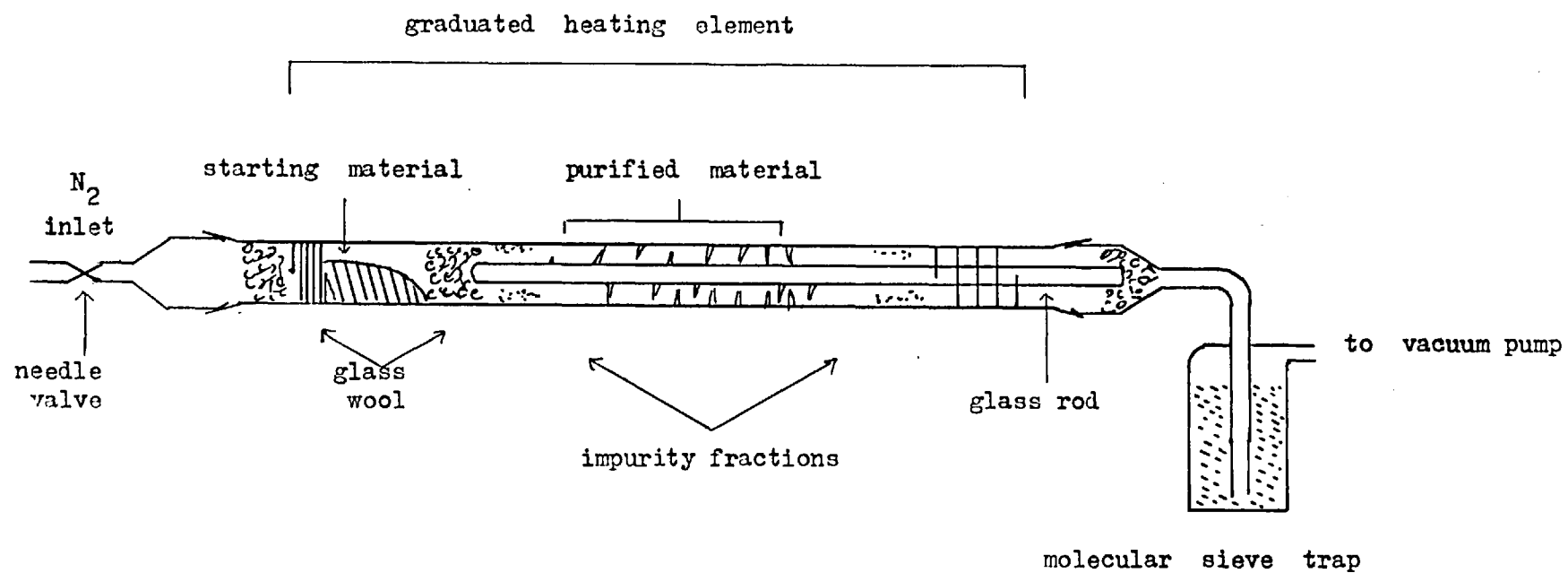


Fig 2.2 - Vacuum sublimation apparatus

described below in an effort to detect any compounds with non-centrosymmetric structures.

2.2.1. The Giebe-Scheibe test for Piezoelectricity (Cady (1964))

A Wayne-Kerr resonance bridge was used to supply an alternating voltage of variable frequency to a sample cell containing small crystals held between two flat electrodes. Any piezoelectric resonances were detected by a coupled variably tuned circuit and amplified to give an audio signal.

This method of testing was only partially successful. The detectivity of the apparatus was very sensitive to the sizes and shapes of the sample crystals, and the responses were generally small, e.g. MNA samples had to contain equant crystallites of the order 10 mm^3 in size before registering a positive result. The magnitude of the response varied greatly between different samples of the same material and therefore results were only qualitative. For comparison, samples of potassium dihydrogen phosphate (KDP) and strontium formate were tested and these crystals gave very strong signals. The implication that none of the organic materials tested were strongly piezoelectric was encouraging because, as was stated in Chapter 1, freedom from piezoelectric resonances is advantageous for an electro-optic material.

On the whole, the test for piezoelectricity was not considered a very useful method of testing for non-centrosymmetric structures because negative results were inconclusive. The three compounds which gave a positive result are labelled with an asterisk in Table 2.2.

2.2.2. Pyroelectric Testing

Pyroelectricity is a spontaneous generation of charge on a crystal surface resulting from a change in the crystal's temperature. The phenomenon can only occur in structures having a polar axis of symmetry; since all such structures are non-centrosymmetric, a demonstration

of pyroelectricity shows a material to be non-centrosymmetric. Conversely, not all non-centrosymmetrics have polar axes and some useful materials could escape detection in a pyroelectric test.

Pyroelectric effects were observed by visual inspection in metanitroaniline and 4-nitrophenylhydrazine. Small needle and platelet crystallites of these compounds were seen to adhere together and to the walls of their storage jars, presumably by electrostatic forces due to charges generated during small temperature variations.

Attempts were made to devise a sensitive test for pyroelectricity which could be applied to all the compounds in Table 2.1. However, initial results were unreliable and further work was not justified because the non-polar non-centrosymmetrics could never be detected by a pyroelectric test however sensitive.

2.2.3. S.H.G. Testing

The method used here was similar to that of Kurtz and Perry (Kurtz (1968)). The beam of a Q-switched Nd:YAG laser was deflected onto small, microcrystalline or powder specimens supported on adhesive tape, and any green light emitted was observed visually. Nineteen materials gave a positive result and these are arranged in Table 2.2, in order of intensity of green emission for a constant input energy. Relative "S.H.G. efficiencies" were calculated from the threshold pulse energy required to produce a visible second harmonic under these conditions.

$$\text{S.H.G. efficiency, } S, = \frac{E_{\text{MNA}}}{E_{\text{S}}}$$

where E_{MNA} = threshold pulse energy required for S.H.G. in MNA

E_{S} = threshold pulse energy required for S.H.G. in the sample.

<u>Material</u>	<u>Relative S.H.G. efficiency</u>
4-nitrophenylhydrazine (NPH)*	1.6
3-nitroaniline (MNA)*†	1.0
1-formyl 2-(4-nitrophenyl)hydrazine (FNPH)*	1.0
4-hydroxyazobenzene	0.8
acetophenone 4-nitrophenylhydrazone	0.8
4-nitrophenol	0.7
benzaldehyde 4-nitrophenylhydrazone	0.6
2-methyl 3-nitroaniline (2MMNA)	0.5
1,4-naphthoquinone	0.4
1,3-dinitrobenzene†	0.4
2,4-dinitro 2'-methoxydiphenylamine	0.4
acenaphthene picrate	0.4
4-amino azobenzene	0.2
2,4-dinitro 3'-methyldiphenylamine	] < 0.2
N,N,-dimethyl 4-nitroaniline†	
3-nitrophenol †	
3-aminophenol	
phthalodinitride	
benzil †	
potassium dihydrogen phosphate (KDP)	

*Positive piezoelectric signal given on Giebe-Scheibe testing

† Previously reported as non centrosymmetric (Stevenson (1970))

Table 2.2. Results of S.H.G. and Giebe-Scheibe testing

In each case, the total pulse energy was measured using an E.G.+G. SGD 100 photo-diode. An absolute value for W_{MNA} , the average power density of the pulse E_{MNA} is estimated here:

$$\begin{aligned}
 W_{MNA} &= \frac{kV}{At} & t = \text{Pulse duration} &= 15 \text{ nS} \\
 &= 1.6 \text{ MW cm}^{-2} & A = \text{Beam area} &= 0.3 \text{ cm} \\
 & & K = \text{Energy meter conversion factor} &= 191 \text{ mJ V}^{-1} \\
 & & V = \text{output of energy meter} &= 0.04 \text{ V}
 \end{aligned}$$

It is emphasised that the above results are only semi-quantitative, because the samples varied considerably in crystallite size and shape. Statistically the results show at least a 32% occurrence of non-centrosymmetric structures among the chosen samples. This value falls between estimates of 42% - based on structures reported in the literature (Rez (1960)) and 25% - based on observation of S.H.G. in powder samples, similar to this work (Southgate and Hall (1972)).

The orders of merit given in Table 2.2 are only a rough indication of the harmonic conversion efficiencies at 1.06 μ . Time did not allow a complete investigation of the electro-optic properties of all the compounds showing S.H.G.; for a direct electro-optic evaluation, an optical quality crystal had to be grown, oriented, cut and polished into cubes of at least 2mm edge length. Since crystal growth of this group of compounds proved more difficult and time consuming than was originally envisaged, effort was directed at 4-nitrophenylhydrazine (NPH), the best observed second harmonic generator and 2-methyl 3-nitroaniline (2MMNA) on which crystal growth studies were already in progress following the discovery of its piezoelectric properties.

2.3. Preliminary Crystal Growth Studies

2.3.1. 2MMNA (2-methyl 3-nitroaniline)

2MMNA was first purified by vacuum sublimation, during which clear yellow needles up to 5 mm long, 0.5 mm wide, were produced. Since attempts at growth from the melt and from acetone solution gave only small fine needles, growth by vapour transport was the most attractive possibility.

A method of vapour growth developed for the growth of MNA (Ayers (1972)) was applied to 2MMNA. Purified 2MMNA was sealed into a glass tube which was immersed in a thermostatically controlled oil bath, set just below the melting point 89.9°C . One end of the tube was slowly pulled out of the bath, this end being cooled by conduction via the brass support rod (Fig. 2.3). The fine taper at the upper end collected a small quantity of supercooled liquid in which a single seed could be formed then carefully allowed to grow. In the case of MNA all the liquid in the taper was solidified onto the single seed, after which growth of a larger, smooth-surfaced boule directly from the vapour was effected by slow withdrawal of the capsule from the bath. However for 2MMNA, lateral growth was extremely slow; a fine needle grew through the liquid and the needle habit persisted during vapour growth.

During both the seeding stage and the growth stage, the pulling rate had to be very slow to avoid re-nucleation and the cooler end of the needle. To counteract the accumulation of impurities formed by thermal decomposition during the long growth runs, the capsule design was modified to accommodate a sidearm for continuous pumping away of impurity vapours. This precaution extended the acceptable duration of a growth run to 3 months, after which had grown a crystal measuring 12 mm x 4 mm x 2 mm.

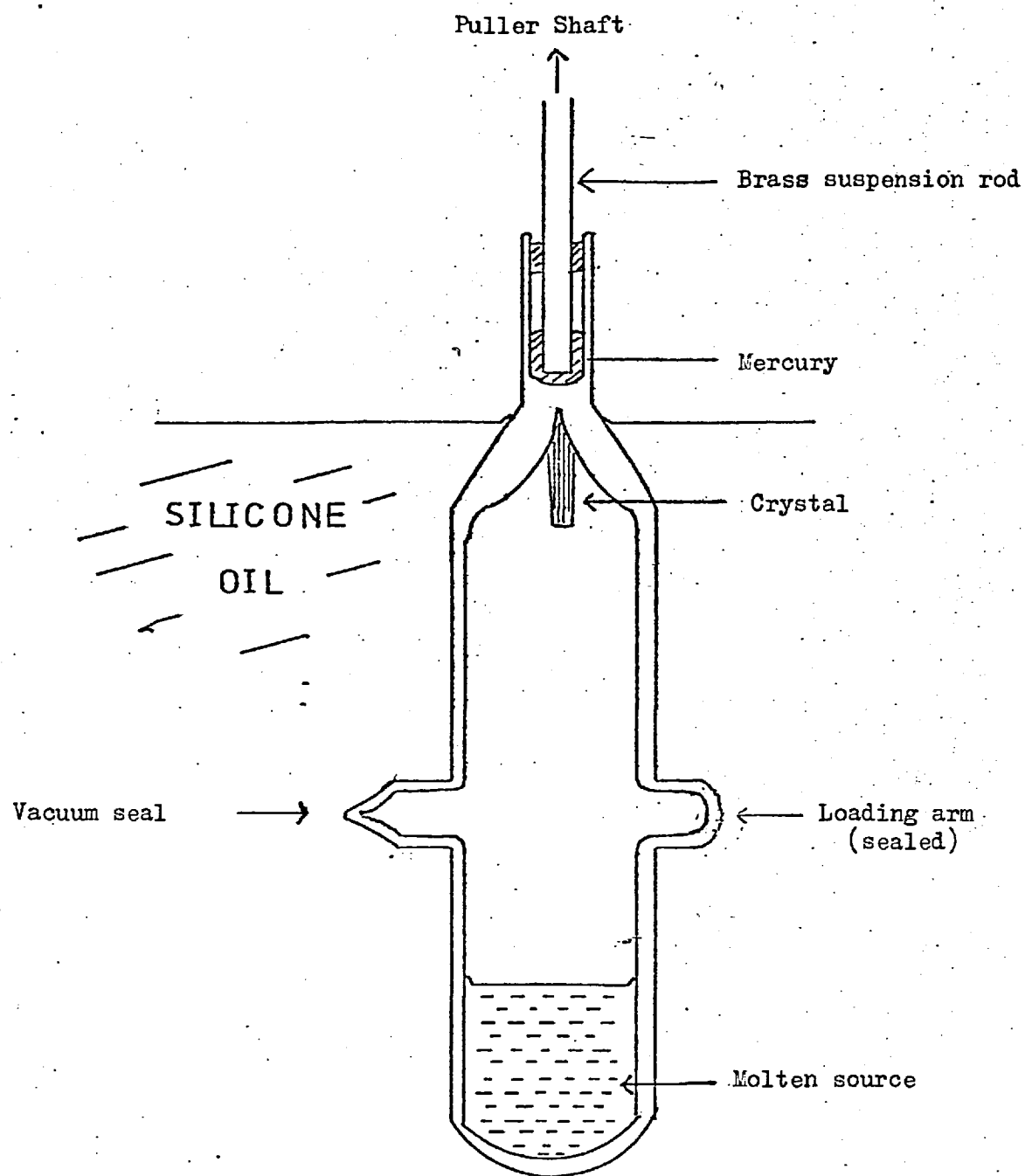


Fig. 2.3 - Vapour growth capsule

2.3.2. NPH (4-nitrophenylhydrazine) and FNPH

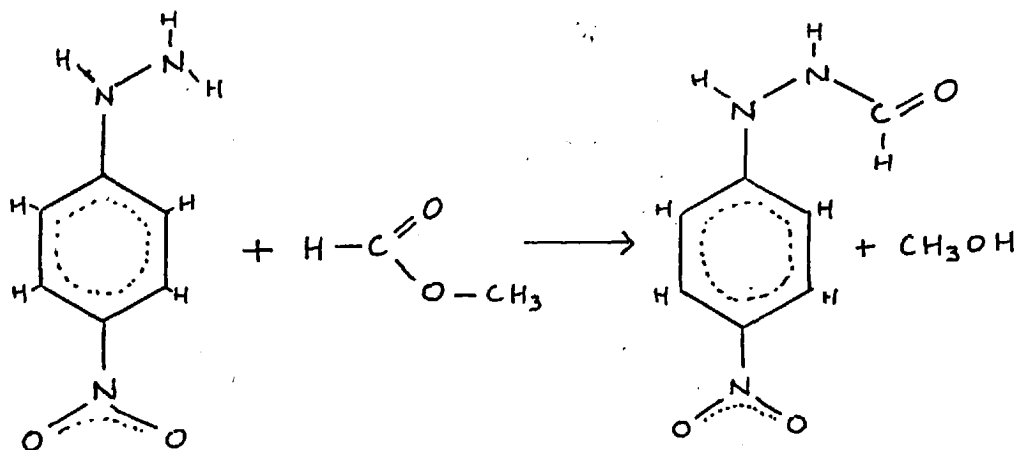
A short investigation of the properties of NPH showed that crystal growth was difficult. Zone refining and melt growth were impossible because of the rapid decomposition of the solid at its melting point (158°C). Vacuum sublimation was partially successful, producing highly strained orange-red crystals measuring about 2 mm x 1 mm x 0.2 mm, but the process gave a quantitative yield of only about 5% because of extensive thermal decomposition. The remaining method, growth from solution, presented problems in the choice of a suitable, non-reacting solvent. One such solvent was ethyl alcohol, but even alcoholic solutions in the absence of oxygen slowly darkened, indicating decomposition. In all the experiments, the rate of decomposition exceeded the maximum growth rate achieved, and attempts were finally abandoned.

During the course of the above experiments, an attempt to grow NPH from a solution in methyl formate produced well formed pale yellow crystals. These were originally thought to be a modified form of NPH, but on chemical analysis were found to be a different substance. A similar preparation reported in the chemical literature (Ruzicka (1946)) describes a compound 1-formyl 2-(4-nitrophenyl) hydrazine with a melting point identical to that of the crystals prepared here, 182-183°C.

Elemental analysis gave the following results:

	Calculated as $C_{17}H_{17}N_3O_3$	Found
C	46.4%	46.62%
H	3.87%	3.85%
N	23.2%	23.21%

The reaction is thought to be:



The substitution of a formyl group onto the nitrogen atom made FNPH much more stable than NPH. Although the crystal structure had clearly been altered, piezoelectric and S.H.G. tests gave positive results. Therefore FNPH was a valuable alternative to NPH, which was difficult to grow in suitable crystals for electro-optic tests. The best method of crystal growth appeared to be growth from solution in ethyl alcohol - a low vapour pressure and high decomposition rate at the melting point rendered vapour sublimation ineffective.

2.4. Space Group Determinations

Concurrently with the above growth studies, crystallographic measurements were made on 2MMNA, NPH and FNPH. The technique used was the Weissenberg moving film method (Henry (1960)). To resolve ambiguity in the last two space group determinations, the absence of a centre of symmetry (verified by S.H.G.) was assumed.

2.4.1. 2MMNA

Needle-shaped crystals suitable for mounting on silica fibres were obtained by vacuum sublimation. A mounted crystal was oriented in the oscillation camera with its needle axis parallel to the

oscillation axis, this being arbitrarily called the c-axis. A simple 300° oscillation photograph using Ni filtered Cu K radiation produced good layer lines whose spacing was measured to give the c-axis lattice parameter. The zero and first order lines were then expanded by the moving-film method to give hko and hkl patterns respectively. The three photographs together gave the following data:

$$\begin{array}{lcl} a = 14.4 \text{ \AA} \\ b = 13.1 \text{ \AA} \\ c = 3.90 \text{ \AA} \end{array} \left. \vphantom{\begin{array}{l} a \\ b \\ c \end{array}} \right\} \pm 1\% \quad \begin{array}{l} \text{Systematic absences } h00 \text{ (} h = 2n + 1 \text{)} \\ \text{oko (} k = 2n + 1 \text{)} \end{array}$$

The two screw axes implied by the absences defined a third screw axis and therefore the space group assigned is $P2_12_12_1$.

A measurement of the density by flotation gave a value of approx. 1.4 g cm^{-3} which agrees with the value calculated from the lattice parameters assuming four molecules per unit cell.

2.4.2. NPH

Vapour sublimation again provided the best crystals for crystallographic measurements. With crystals mounted on an arbitrary c-axis, the diffraction photographs, taken as for 2-MMNA, were in this case ambiguous as the crystals were highly strained and in platelet form. An interpretation of the results is given here;

$$\begin{array}{l} \text{Systematic absences } hko \text{ (} h = 2n + 1 \text{)} \\ \text{okl (} k = 2n + 1 \text{)} \end{array}$$

$\therefore$ space group is $Pb2_1a$ - $Pca2_1$ on transformation of axes choosing c as the polar axis

$$\left. \begin{array}{l} a = 12.5 \text{ \AA} \\ b = 3.75 \text{ \AA} \\ c = 14.7 \text{ \AA} \end{array} \right] \pm 2\%$$

experimentally determined density = 1.53 g cm^{-3} ,

This gives 4 molecules per unit cell.

2.4.3. FNPH

Good crystals were obtained from a saturated solution of FNPH in 60°C ethanol, slowly cooled overnight. The diffraction photographs were taken as for 2MMNA again calling the oscillation axis c.

Systematic absences $h0l$ ($h = 2n + 1$)

okl ($l = 2n + 1$)

$\therefore$ space group is $Pca2_1$

$$\left. \begin{array}{l} a = 10.3 \text{ \AA} \\ b = 9.5 \text{ \AA} \\ c = 8.0 \text{ \AA} \end{array} \right] \pm 1\%$$

experimentally determined density = 1.53 g cm^{-3} .

This gives 4 molecules per unit cell.

Conclusions

This preliminary investigation proved extremely useful in having demonstrated second harmonic generation in nineteen compounds; fourteen of these have not been previously reported as non-centrosymmetric. These compounds are very worthy of further study

as they have potential uses as pyroelectric, piezoelectric and non-linear optical crystals.

Of particular interest to theoreticians may be 2MMNA, which have a molecular structure very similar to MNA, on which some electro-optic data are available (Stevenson (1973)). 2MMNA was shown to crystallize in a different space group to MNA, and therefore a comparison of electro-optic data between the two materials may yield valuable information about the effect of the lattice on the electro-optic coefficients.

NPH would be of exceptional interest practically if a successful method of crystal growth could be applied to it. The second harmonic generation tests on microcrystalline specimens showed it to be more efficient than MNA, which has large non-linear susceptibility coefficients (Southgate (1972)).

Within this project, time only allowed systematic crystal growth and electro-optic evaluation programmes for one material, and work proceeded exclusively on FNPH, which, from the S.H.G. results, could be expected to have an electro-optic effect similar to MNA.

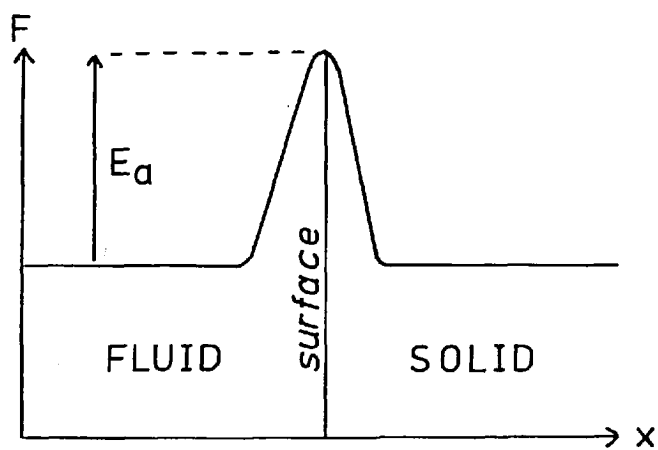
CHAPTER 3 - CRYSTAL GROWTH OF FNPH

Introduction

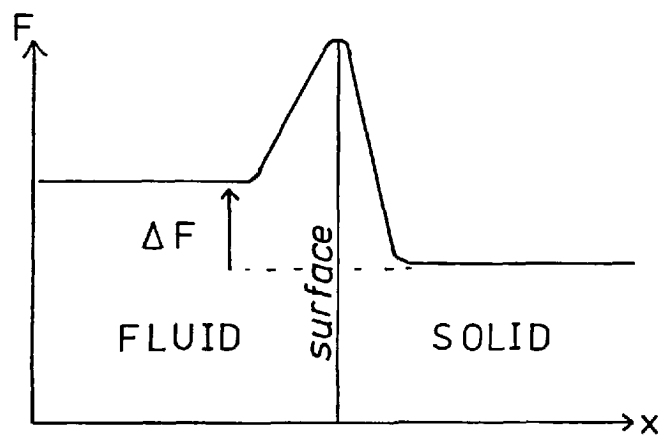
The only feasible method of growth of FNPH is growth from solution, because the solid has a low vapour pressure and decomposes rapidly above its melting point. An account of the methods and results of the experiments on crystal growth will be given later in the chapter, but first an account of the relevant theory will be given.

Mathematical models have been applied to the crystal growth process and these appear in some reviews, e.g. Strickland-Constable (1968), Brice (1973). For vapour-solid systems simple models can successfully predict growth parameters (Faktor (1974)), but in solution systems the mathematics becomes more cumbersome (Ohara (1973)). In the case of FNPH, the complexity of the model would probably be prohibitive, and any quantitative results would be of academic use only, because of the lack of experimental data to determine the model parameters. In view of this, the following will be a qualitative account of the basic principles which apply to solution growth.

Disregarding for the moment the molecular approach, the growth process is treated as a change of phase from fluid to solid. A very important parameter is the transition point, described as the temperature, pressure and concentration at which both phases exist in dynamic equilibrium. This is illustrated in Fig. 3.1 which shows the condition for equilibrium, i.e. that the free energy of a molecule, F , be the same in each phase. If the free energies are not balanced, then only the phase with the lesser energy is stable and total conversion to that phase occurs at a rate determined by kinetic factors. The latter may be described by an activation energy, E_a , which determines the rate of crystallization, f ,



(a) Dynamic equilibrium at the transition point



(b) Crystallization below the transition point

Fig. 3.1- Energy diagrams of the fluid / solid interface

$$f \simeq A \exp \left(- \frac{E_a}{kT} \right) \quad (3.1)$$

where A = rate constant

k = Boltzmann constant

T = absolute temperature.

The denominator kT reduces the effect of the activation barrier at high temperatures where very high growth rates can be achieved.

The transition point is often represented by a phase diagram, e.g. a graph of sublimation temperature against pressure, Fig. 3.2 (equivalently described as vapour pressure versus temperature). The sublimation temperature is not constant because the free energy of a solid molecule is dependent on temperature alone while that of a vapour molecule is a function of temperature and pressure.

A common application of the vapour pressure curve arises in crystal growth from the vapour. Fig. 3.3 illustrates a simple system in which the applied temperature gradient is taken as uniform through the vapour up to the interface, where the equilibrium condition of the actual temperature, T_a , being equal to the sublimation temperature, T_s , is assumed. By removing gas molecules at the surface, the progress of crystal growth sets up a pressure gradient. The latter relates via the vapour pressure curve to the sublimation temperature so that values of T_s may be estimated. The shaded area of Fig. 3.3 clearly represents instability where the actual temperature is below the equilibrium sublimation temperature. This phenomenon is called constitutional supercooling.

The kinetic consequences of constitutional supercooling are now discussed. The extent of positive deviation of T_s from T_a in Fig. 3.3 is a direct indication of the driving force for crystallization, ΔF , (see Fig. 3.1b) This driving force serves to reduce the effective

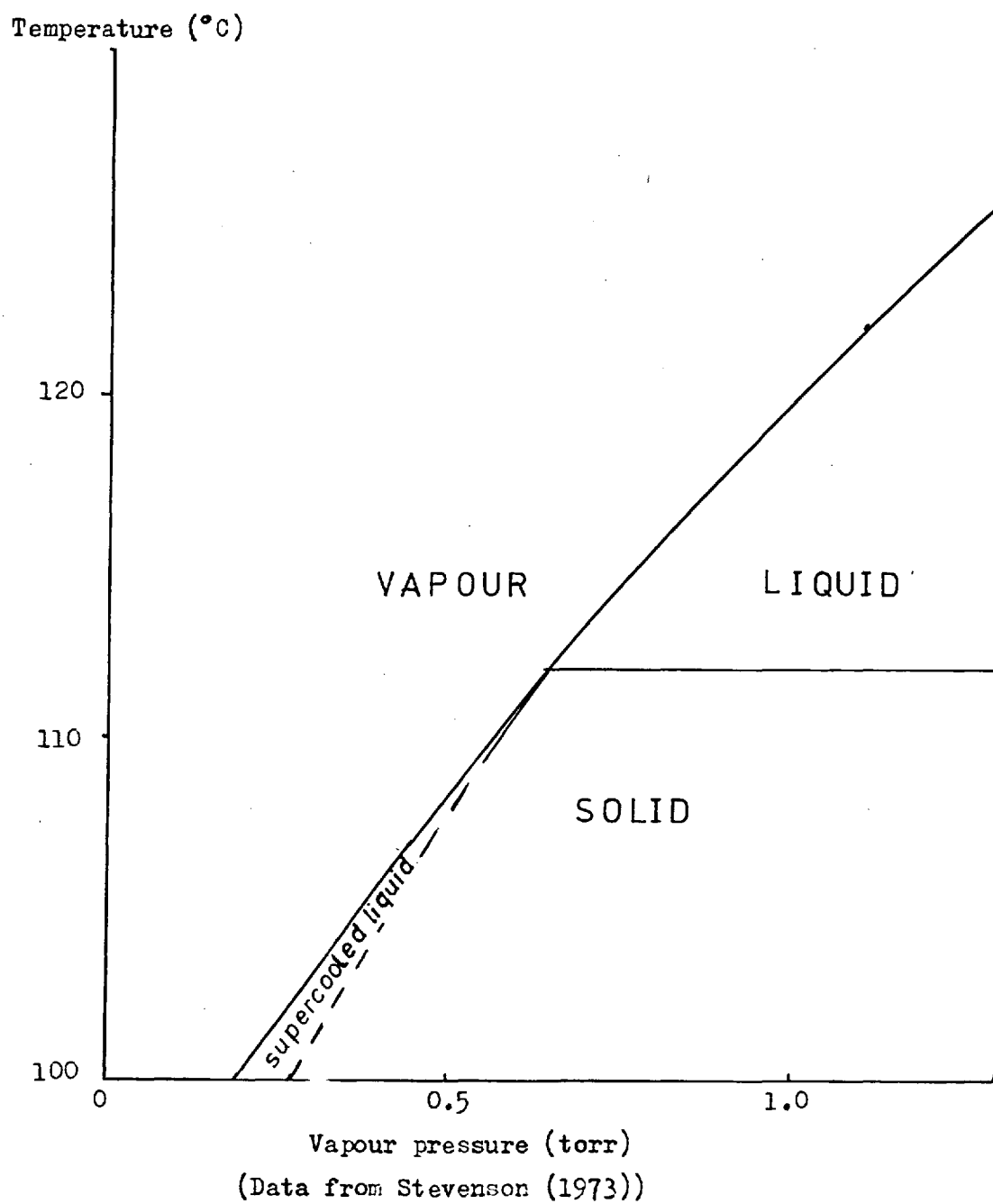


Fig. 3.2 - Phase diagram of 3-nitroaniline

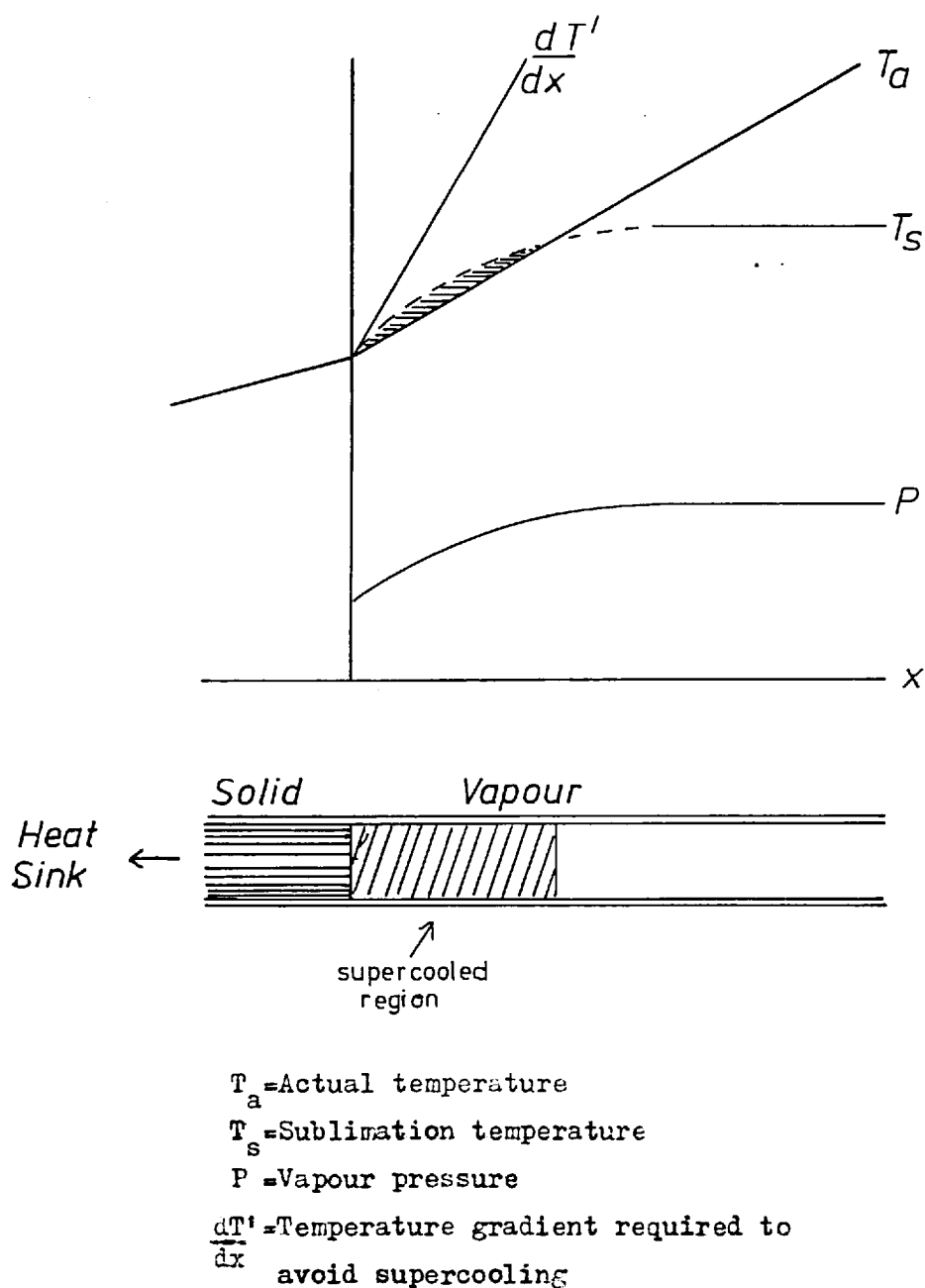


Fig 3.3 - Constitutional Supercooling in a Vapour Growth System

activation barrier E_a such that the rate of crystallization may be expressed in terms of ΔF :

$$f \approx A \exp \left(\frac{\Delta F - E_a}{kT} \right) \quad (3.2)$$

Now we see that the rate of crystallization within the supercooled region is greater than at the interface. An extreme case of constitutional supercooling is the formation of crystals in front of the growing interface. This rarely occurs in practice since nucleation demands a much higher activation energy than growth so the interface is relatively stabilized. A more common result is 'interface instability', where an irregularity of the surface is amplified during growth (Fig. 3.4).

In the vapour growth system illustrated, constitutional supercooling can be eliminated simply by increasing the temperature gradient to the value of $\frac{dT'}{dx}$ shown in Fig. 3.3. Provided no other complications arise, the growth interface should follow the isothermal surface $T = T_s$ and the resulting crystal will have a smooth surface, continuous in the mathematical sense.

Not all crystals grow with an isothermal surface - in many cases the surface is interrupted by facets, regions which need various degrees of supercooling before growth occurs. This is a kinetic rather than thermodynamic limitation - F for the bulk solid is the same regardless of the growth habit, but the activation barrier E_a may change from one facet to the next. The origin of a variable energy barrier becomes evident on examining the system on a molecular scale. A molecule on the surface of a solid will have a different free energy to that of the bulk molecule which was used to define F . The free energy of a molecule breaks into two components:

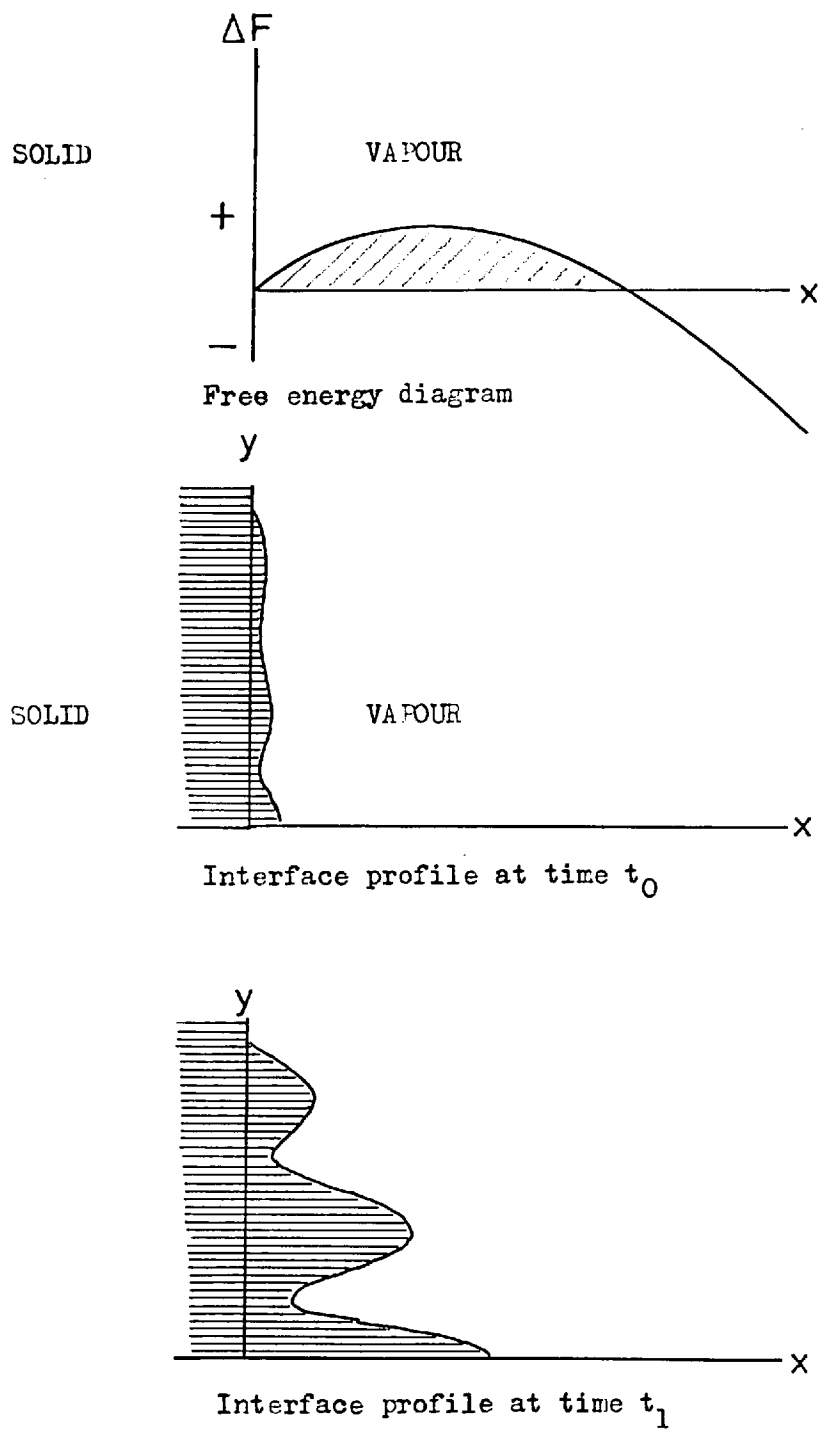


Fig. 3.4 - Interface instability caused by constitutional supercooling

$$F = E - TS \quad (3.3)$$

E represents the total energy derived from chemical bonds to neighbouring molecules in the solid. The entropy, S , represents the positional freedom allowed the molecule, which is greater in the fluid state. The two factors balance at the transition point so that F is the same for solid and fluid. For the surface molecule, F may exceed this value since the surface offers less freedom than the fluid phase and fewer bonds than the bulk solid. The surface molecule is thus activated. The height of the activation barrier varies for different types of sites on the surface as shown in Fig. 3.5 and also for different surfaces, Fig. 3.6. The rough interface has a low activation barrier, and therefore would exhibit an isothermal surface; the smooth interface has a high activation barrier causing faceted growth. A semi-quantitative description of surface roughness has been proposed by Jackson (1967), involving a factor α , where

$$\alpha = \frac{\Delta H}{kT_m} \left(\frac{n'}{n' + n} \right)$$

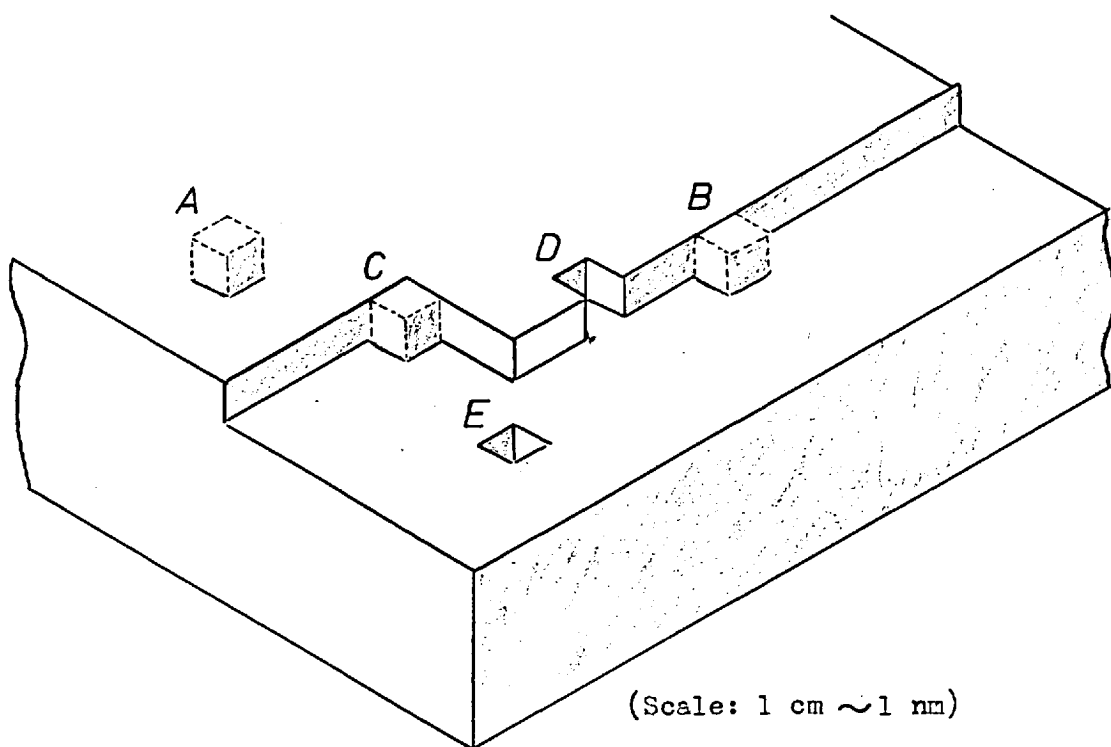
where ΔH = heat of transition

T_m = transition point

n = total energy of bonds parallel to surface

n' = total energy of bonds perpendicular to surface.

The above theory is now applied to the growth of crystals from solution. Conventional solution growth does not employ a temperature gradient - the whole solution is supercooled. The situation is illustrated in Fig. 3.7a, which is analogous to Fig. 3.3, omitting the temperature gradient and substituting for the sublimation temperature a saturation temperature derived from the solubility curve. The latter may have a



Site free energies $A > B > C > D > E$

Fig 3.5 - Schematic representation of a crystal surface

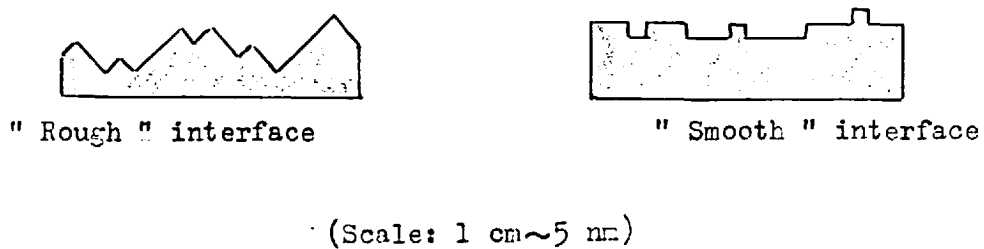
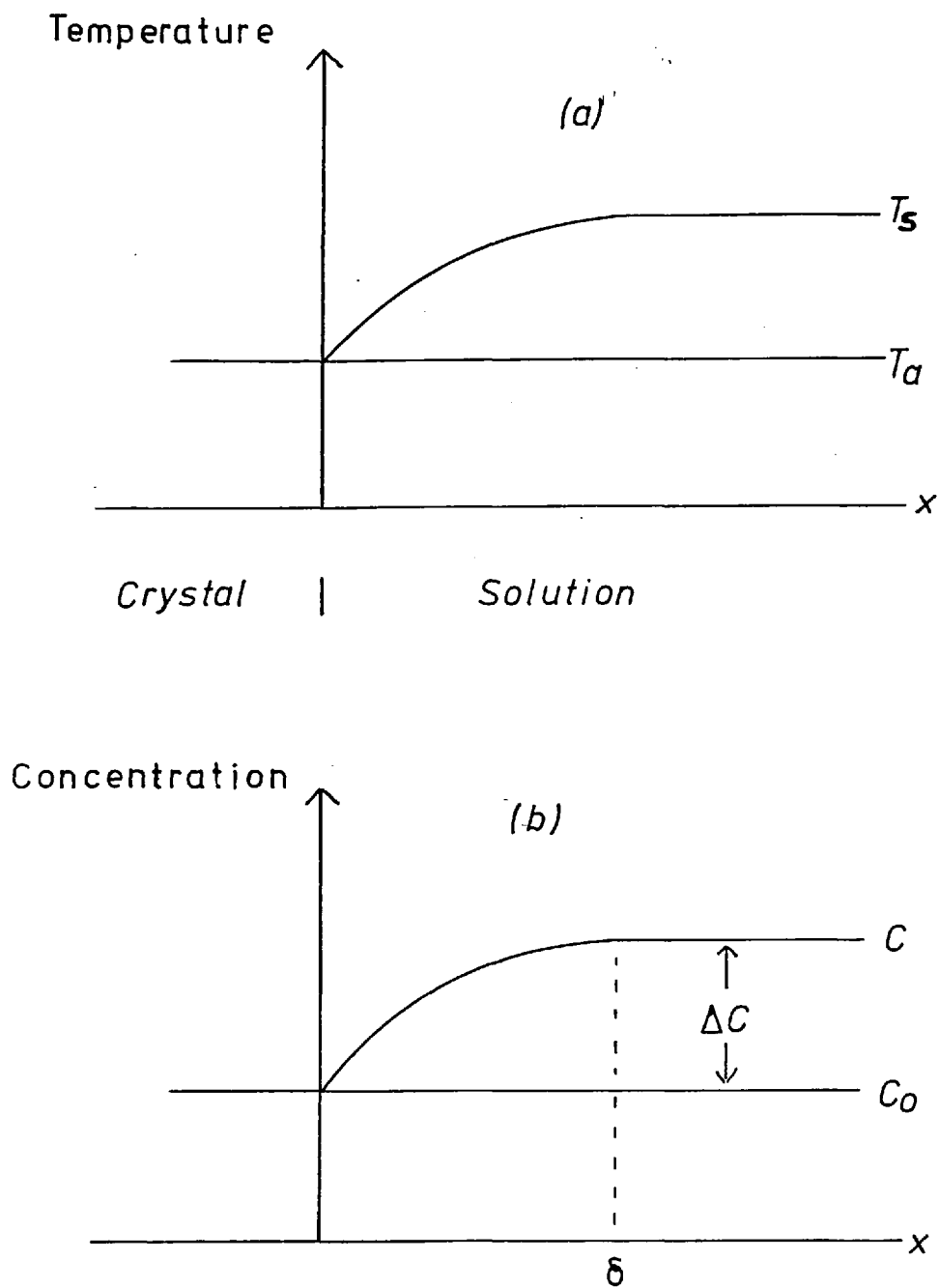


Fig. 3.6 - Crystal surfaces in profile



T_s = Saturation temperature

T_a = Actual temperature

C = Actual concentration

C_0 = Concentration of a saturated solution

δ = Boundary layer thickness

Fig 3.7 - Constitutional supersaturation in
Solution Growth

negative slope, so the general case is better described here in terms of concentration, as in Fig. 3.7b, where F is represented by the supersaturation, ΔC . Constitutional supersaturation is now inevitable and a high activation energy associated with the facet is important in providing stabilization.

The two mechanisms of interface stabilization are directly compared in Fig. 3.8. At high temperatures, where the effect of the activation barrier is reduced, the temperature gradient method may prove useful in providing stability. This has been demonstrated in the case of liquid phase epitaxy of garnets at 1000°C (Davies (1974)). At low temperatures, however, facet stabilization is dominant and isothermal growth by application of a temperature gradient has not yet been attempted.

Corresponding to the activation energy of each facet there is a value of supersaturation which, if exceeded, would cause instability. For a rough interface this supersaturation can be very low, so that growth on other facets with smooth interfaces is very slow or even non-existent. Sometimes the problem is insuperable and needle or plate shaped crystals will grow; in other cases Nature is more lenient and forces rough surfaces to "grow out", e.g. the (001) face of KDP, Fig. 3.9.

Compared with the stabilization of an interface by temperature gradation the stability of facets is difficult to control experimentally. The activation parameter used above is a simple concept used to describe a very complex mechanism of growth. In reality, the relative stability of different facets may be changed by different conditions, e.g. supersaturation, temperature, addition of impurities.

The rate of growth is controlled by two factors - transport of solute from the bulk of the solution to the interface and the incorporation

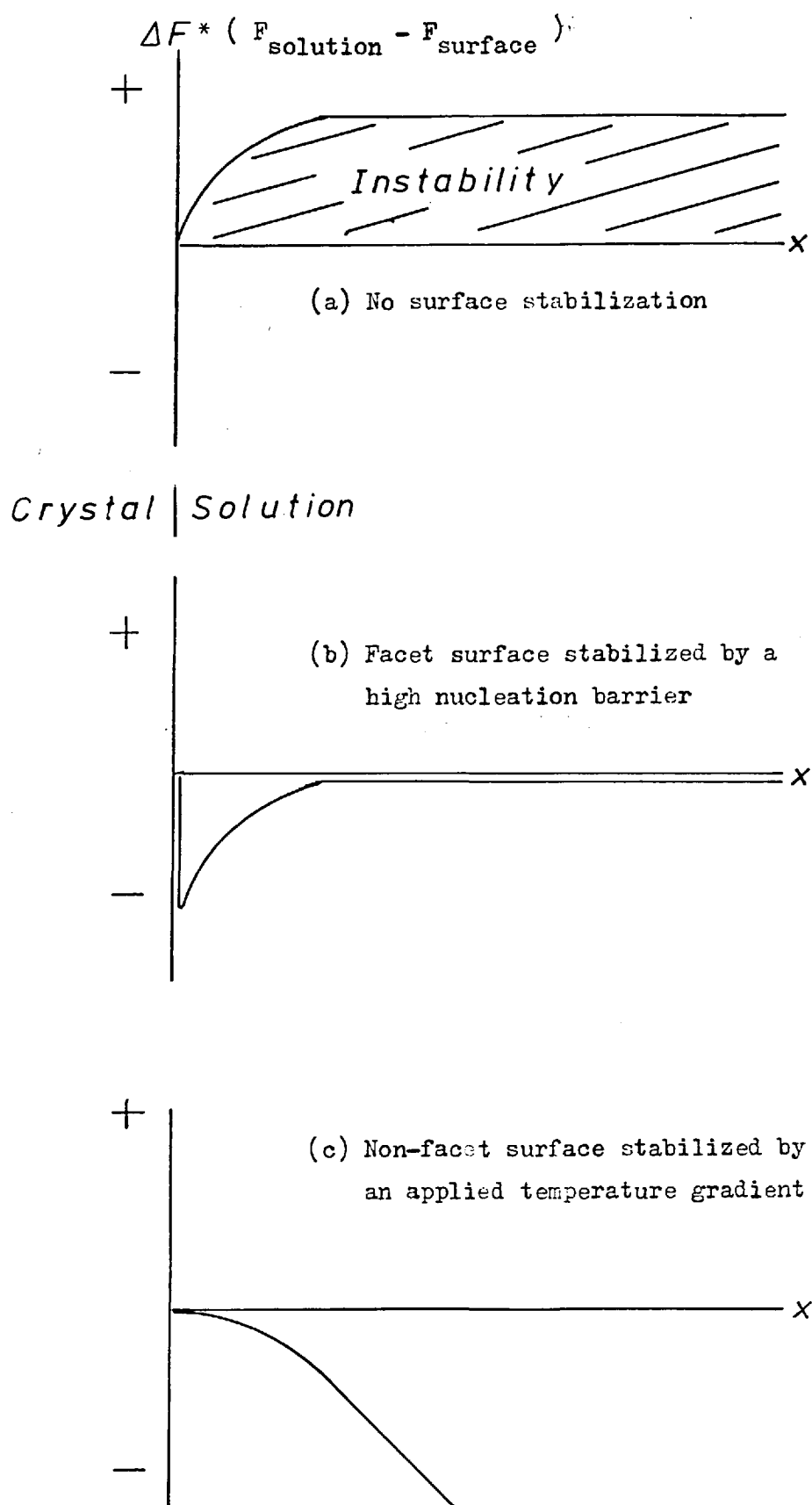
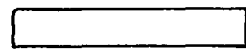


Fig.3.8 - Interface stability in solution growth



(a) Initial seed has (001) face exposed.



(b) Extreme interface instability occurs.



(c) Stable $\{101\}$ form develops but the underlying "cap" contains voids.



(d) $\{101\}$ has nearly eliminated (001) .



(e) Clear growth begins on $\{101\}$ faces.

Fig. 3.9 - Growth of KDP onto its (001) face

of molecules into the crystal at the interface. The former is dependent on the hydrodynamics of the system. It may be shown that the change in concentration from the solution bulk to the interface occurs mainly across a narrow region near the interface, provided that the solution is stirred. This region is called the boundary layer and its thickness, δ , (see Fig. 3.7) is a decreasing function of the solution flow velocity (Carlson (1958)). For a given concentration difference across the boundary layer, the rate of solute transport is inversely proportional to the boundary layer thickness, which is minimized by efficient stirring. The second limiting factor, the rate of incorporation of molecules into the crystal, is not so easily analyzed and requires a complex statistical treatment even in the simplest cases. An additional complication can arise in the case of organic compounds; this is the re-orientation required of a highly asymmetric molecule before incorporation may occur. It is sufficient here to state that this step can cause a severe limitation to the maximum growth rate.

The relatively slow rates of growth observed for some organic compounds can cause practical problems. Not only must the apparatus for temperature control (see below) function continuously for a longer period, but also stringent precautions must be taken to avoid decomposition or oxidation of the solute. Some precautions which may be taken are:

- (1) Exclusion of impurities which might catalyse decomposition.
- (2) Use of an inert atmosphere and a chemically inert solvent.
- (3) Protection from strong light.

The field of organic compounds chosen for this study was, for the reasons explained in Chapter 1, that of molecules with an electron donating and an electron accepting group substituted on an aromatic ring. Such a combination of reducing and oxidizing groups, when given

the orientation freedom provided by the solution state, is prone to auto-oxidation.

Whatever the precautions taken, some decomposition inevitably occurs during a long growth programme. In this case, a compromise must be made between a high supersaturation, which gives rapid growth but strained crystals, and a low supersaturation, which generally decreases strain but limits the size of crystal grown before deterioration of the solution.

A similar compromise must be found for the optimum growth temperature - a high growth temperature facilitates crystallization but also accelerates decomposition.

3.1. Apparatus for solution growth

Solution growth is exceptional in crystallization because the solution contains a large proportion of solvent which is rejected at the interface thus making efficient mass transfer essential. In low temperature work this is most easily achieved by stirring. A well-tried system is the Holden Rotary Crystallizer (Holden (1949)) on which the design of apparatus used in this work was based. The solution is held in a cylindrical container and agitated by radial paddles, on which seed crystals are mounted, connected to a rotating central shaft. Flow in the vertical direction is achieved mainly by natural convection in the Holden crystalliser - here it is aided by centrifugal force since the paddles are positioned near the solution surface (Fig. 3.10).

Some other modifications to the Holden design were made. Because of a need for scaling down in size, the vessel was partially immersed in a thermostatically controlled oil bath whose large thermal mass increased the thermal stability of the system. Heating from below was retained as it provided natural convection and desaturated the solution

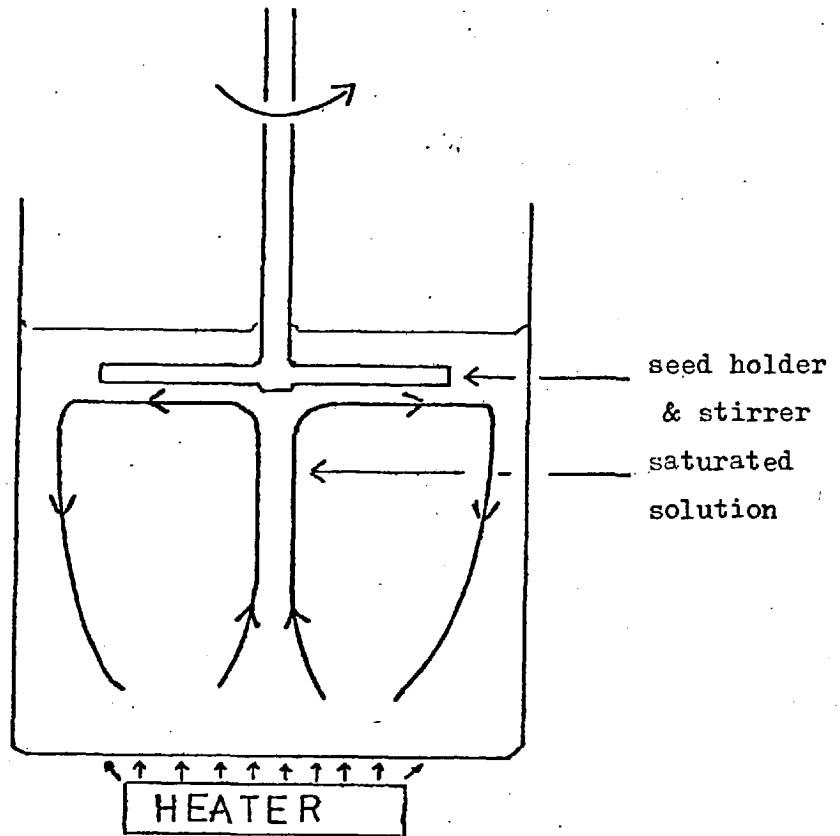


Fig 3.10 - Flow pattern in modified Holden crystallizer

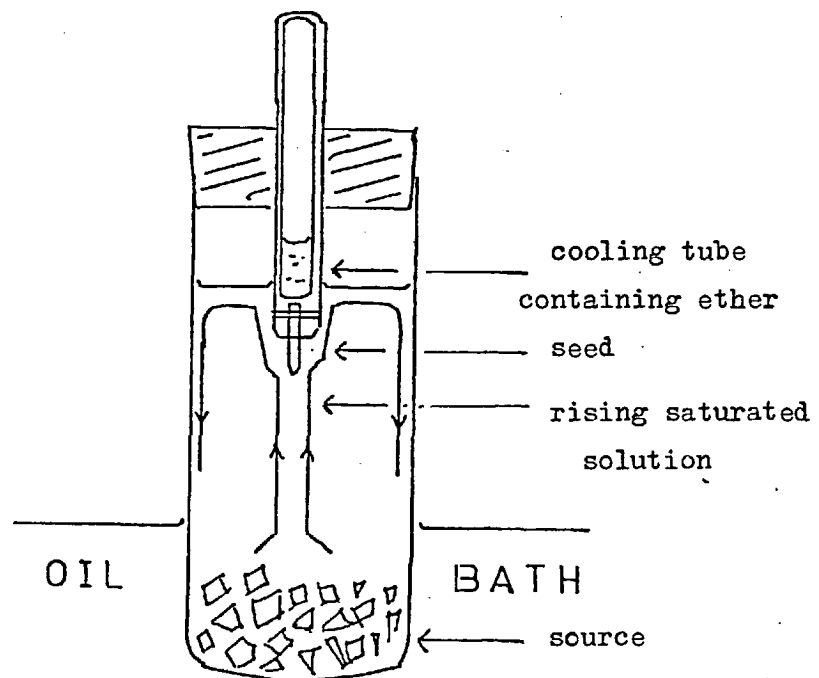


Fig 3.11 - Simple convection apparatus for solution growth

near the tank base where spurious nuclei could otherwise collect and grow. Parasitic growth could also occur on the stirrer shaft and the walls of the vessel - for this reason the apparatus was designed to cause condensation at these regions so that any stagnant solution was continually washed away (Fig. 3.14).

This modified Holden design was used as a basis for the design of three apparatuses described below, in which it gave the necessary control over spatial fluctuations in supersaturation. Temporal control of supersaturation must compensate for the depletion of solute during growth. The growth rate is represented:

$$\frac{dx}{dt} = -k\Delta C^n \quad (3.5)$$

where ΔC = supersaturation

$$\Delta C = C - C_o(T)$$

C = actual concentration of solution

C_o = concentration of a saturated solution

k = rate constant

n = order of reaction (usually $1 < n < 2$)

To avoid interface instability, ΔC must be kept small. In that case, small variations in temperature have a marked effect on the supersaturation - a control of temperature to $\pm 0.01^\circ\text{C}$ should be achieved.

Three methods were used for maintaining a constant supersaturation and these will now be described.

3.1.1. Replacement of solute

A solution of a constant supersaturation may be produced by saturating the solvent by contact with solute at a temperature T_1 , then cooling the solution to a temperature T_2 during transfer to the growing

crystal at this temperature,

$$\Delta c = c_o(T_1) - c_o(T_2) \quad (3.6)$$

The main difficulty arising from this otherwise simple method is the transfer of the solution from source to seed. Two methods were used to achieve this:-

(a) The apparatus of Fig. 3.11 employs natural convection from the heated solution at the lower end of the tube to a seed held at the cool upper end. Small crystals were grown by this method but spurious nucleation on the seed holder impeded growth of large crystals. Had this not occurred, another limitation to the crystal size would have been caused by the unidirectional nature of the convectational flow near the seed - only the lowermost end of the crystal received freshly enriched solution.

(b) A more sophisticated apparatus is shown in Fig. 3.12. The Archimedean pump establishes a flow of solution through the heater tube into the saturation chamber then through the cooling tube into the growth vessel containing seeds mounted on a stirrer paddle. The apparatus gave only limited success because of an undesirable redistribution of solute caused by recrystallization within the saturation vessel.

3.1.2. Removal of solvent

The concentration of the solution was maintained by allowing the solvent to evaporate at constant temperature.

The rate of evaporation was controlled to compensate for the solute depletion caused by growth. The depletion is calculated thus:

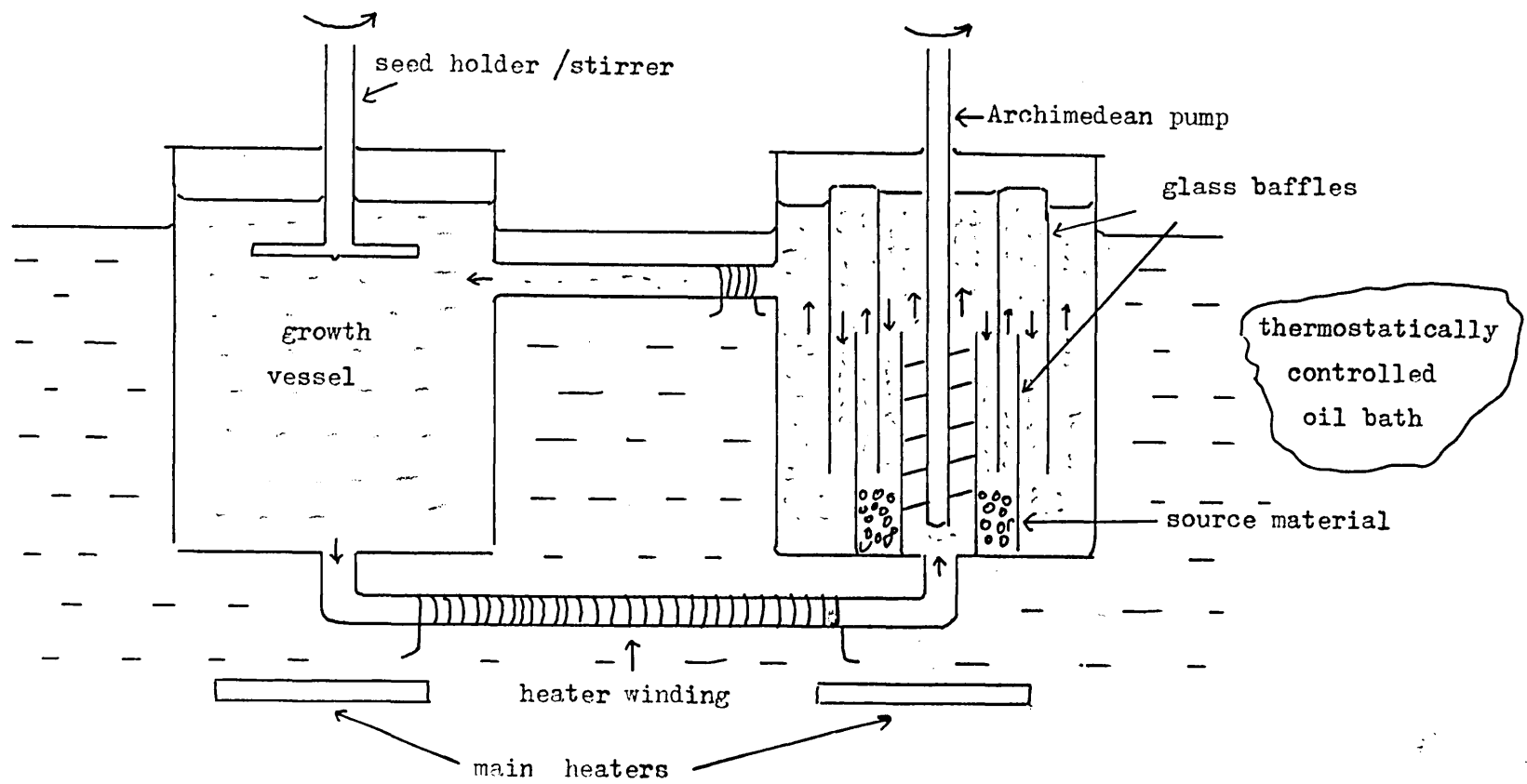


Fig 3.12 - Apparatus for growth by solution circulation

$$C = \frac{m}{V}$$

$$= \frac{v}{\rho V}$$

where m = mass of solute in solution

v = volume of solute

ρ = density of solute

V = volume of solvent

for a constant supersaturation,

$$\frac{dC}{dt} = \frac{1}{\rho} \left(\frac{v dV - V dv}{V^2 dt} \right) = 0$$

$$\frac{v dV}{dt} = \frac{V dv}{dt} \quad (3.7)$$

$$\frac{dv}{dt} = \text{rate of removal of solute}$$

$$= -A \frac{dx}{dt} \quad \text{where } A = \text{area of growing surface}$$

$$= -Ak \Delta C^n \quad \text{from eqn. (3.5)}$$

$$\text{from (3.7)} \quad \frac{dV}{dt} = \frac{V}{v} \frac{dv}{dt}$$

$$= -\frac{Ak \Delta C^n}{\rho C}$$

$$\text{or in general} \quad \frac{dv}{dt} = -\frac{1}{\rho C} \sum_i A_i k_i \Delta C^{n_i} \quad (3.8) \quad \text{where } i \text{ represents one}$$

facet.

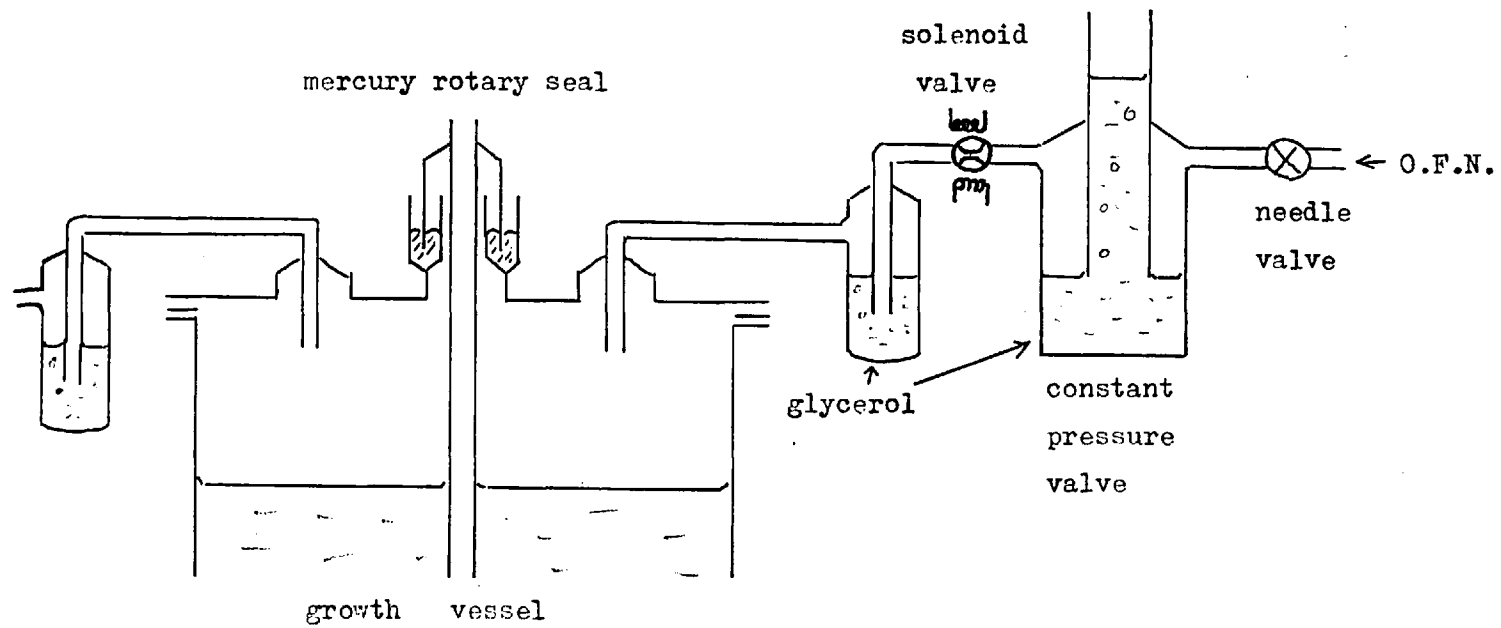


Fig.3.13 - Apparatus for controlled evaporation of a solution

The solvent was to be removed at a rate proportional to the area of growing surface, which increased during growth. The apparatus of Fig. 3.13 was used to expose the solution to a controlled flow of gas in order to achieve a controlled evaporation. The disadvantage of this method was the difficulty in achieving the extremely slow gas flows required at the initial stage. An improvement on this method has been reported in the case of growth from aqueous solution, in which the solvent was removed by electrolysis so that the rate of solvent removal could be controlled electrically.

3.1.3. Change in temperature

Although T should ideally remain constant during growth, it is often found that a variation in T over a small range is tolerable provided ΔC remains constant. This small range of temperature allows the solubility to be approximated to a linear function of T :

$$C_o = \alpha T$$

α is usually positive, i.e. depletion of solute has to be accompanied by a decrease in temperature. A programme for temperature lowering may be calculated thus:

$$\Delta C = C - \alpha T$$

$$\frac{d\Delta C}{dt} = \frac{1}{\rho V} \frac{dv}{dt} - \frac{\alpha dT}{dt} = 0$$

$$\frac{dT}{dt} = \frac{1}{\rho V \alpha} \frac{dv}{dt} = - \frac{Ak \Delta C^n}{\rho V \alpha}$$

$$\text{i.e. } T_t = T_o - \frac{Ak \Delta C^n t}{\rho V \alpha}$$

$$= T_o - \frac{1}{\rho V \alpha} \sum_i A_i k_i \Delta C_i^n t \quad \text{for } i \text{ facets} \quad (3.9)$$

Generally, A will be a quadratic function of t so that the required temperature should be programmed as a cubic function of time.

The apparatus used is shown in Fig. 3.14. A second vessel was used to produce a saturated solution which was pumped into the growth vessel containing seeds. The temperature of the oil bath was then slowly lowered to achieve growth onto the seeds. This system proved the most successful and is described in detail below.

3.2. Experimental Procedure and Results

The method of preparation of FNPH is described in Appendix I.

Subsequent to the preliminary investigations during which FNPH was grown from its solution in ethanol, it was found that the solubility of FNPH and its temperature coefficient were greater in methanol, while the crystals obtained were similar. Methanol was therefore chosen as the solvent for further work. The solubility curve was found by allowing mixtures of FNPH and methanol to equilibrate at various temperatures, filtering through a weighed sintered glass Gooch funnel, then drying and weighing the residue with the funnel. The curve is shown in Fig. 3.15.

From the solubility curve the following information was obtained:-

$$\text{Solubility at } 45^{\circ}\text{C} = 28 \text{ g l}^{-1}$$

$$\text{Average temperature coefficient between } 45^{\circ} \text{ and } 30^{\circ} = 0.9 \text{ g l}^{-1} \text{ }^{\circ}\text{C}^{-1}.$$

Overnight cooling of a solution of FNPH in methanol saturated at 60°C provided suitable seed crystals measuring about 3mm x 1mm x 1mm. Six seeds were mounted on the stirrer paddle using fine platinum wire

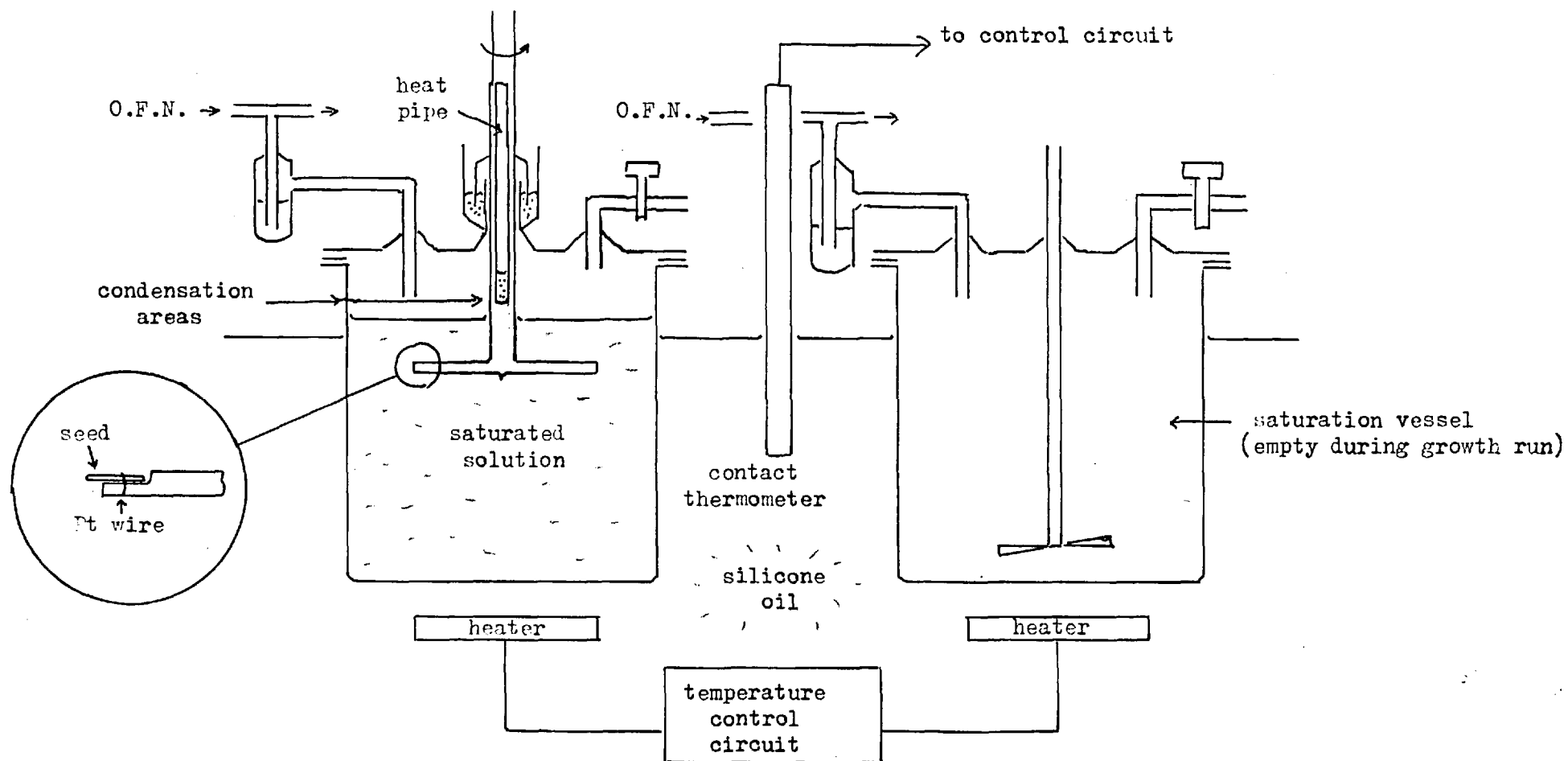


Fig.3.14 - Apparatus for growth by temperature lowering

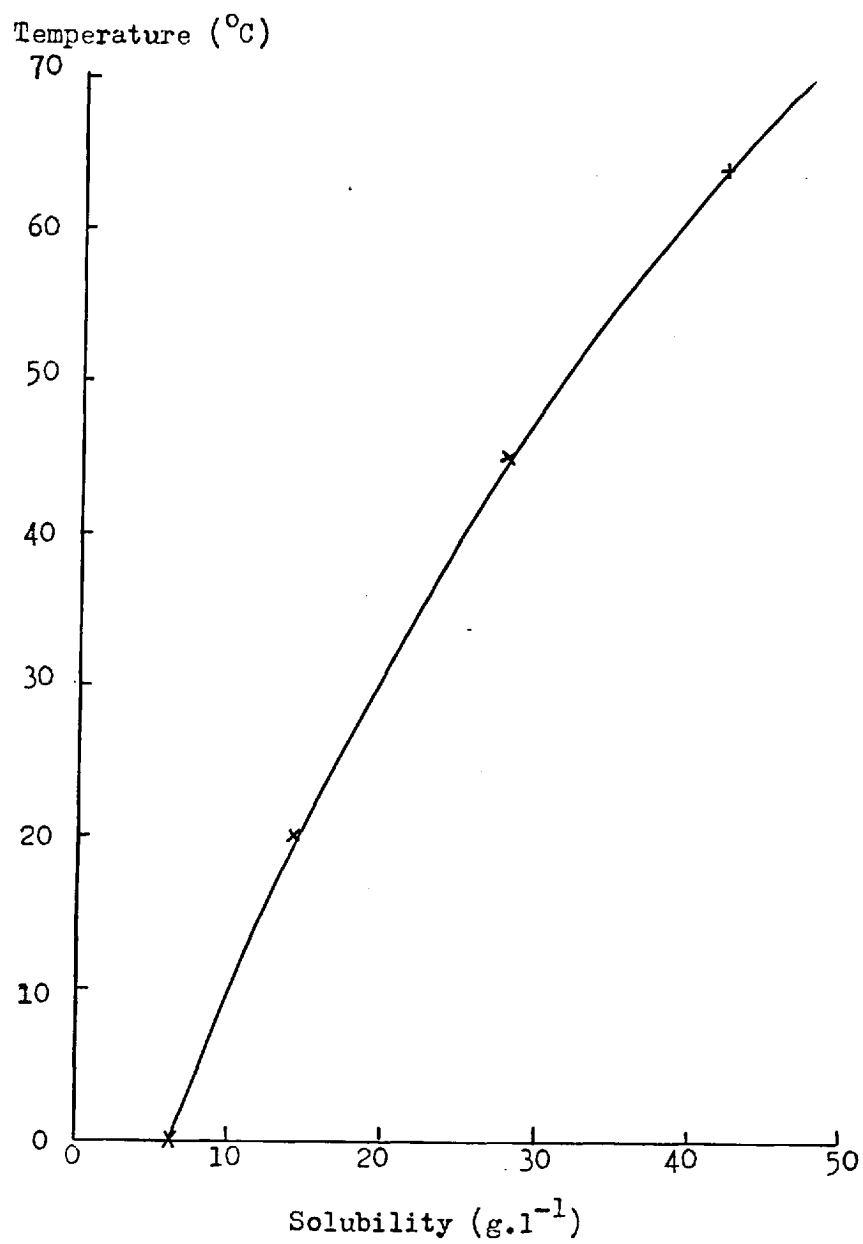


Fig.3.15 - Solubility curve of FNEH

as shown in Fig. 3.14 . With reference to this figure, the left hand tank was cleaned with chromic acid followed by deionised water and then dried. The tank lid with the loaded seedholder was then placed in position. In the right hand tank was placed 30g FNPH and 1 litre methanol. The temperature controller was set at 45°C, the tank flushed with nitrogen and the mixture stirred for two days. The temperature controller was then set at 47°C and the solution quickly pumped into the left hand vessel onto the seeds, leaving any undissolved FNPH in the right hand vessel. The controller was left at 47°C until any solid FNPH at the base of the vessel was completely dissolved and the seeds showed signs of rounding at the edges indicating dissolution (4 hrs.). At this point the temperature controller was set at 44°C and left for one day. A temperature lowering programme of 0.2°C per day was started and continued for 6 days. The expected growth was calculated thus:

$$\Delta T = 2.2^{\circ}$$

$$\begin{aligned} \text{Expected volume of solid crystallised} &= \frac{2.2\alpha}{\rho} = 1.32 \text{ cc} \\ &= 0.22 \text{ cc per seed} \end{aligned}$$

Up to this point no growth had been observed, although the calculated amount of deposition would certainly have been visible had it occurred. After a further three days, when the supersaturation had reached 2.8°C, rapid growth began. This continued for ten days, after which the cooling rate was doubled to allow for the larger area of the seeds and for some parasitic crystals which had formed. This rate of temperature lowering was maintained for another five days, by which time the solution had darkened considerably and the quality of growth

appeared to be deteriorating. The run was then terminated by pumping out the solution, leaving a little in the base of the vessel to maintain an atmosphere saturated with methanol to prevent rapid evaporation of the solution adhering to the crystals. The tank was cooled to room temperature while a gradual flow of nitrogen dried the crystals. The largest single crystal grown (some seeds suffered re-nucleation) is shown in Fig. 4.5 and measured 1cm x 1.8cm x 0.7cm.

3.3. Morphology of FNPB

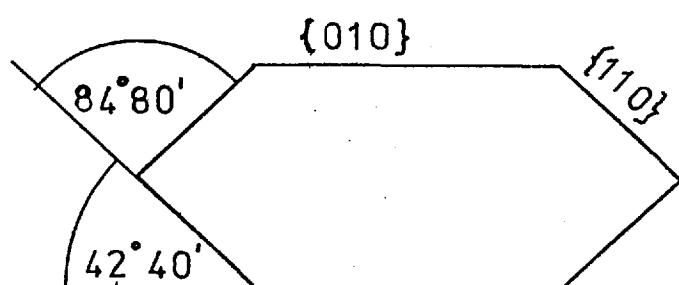
A two circle goniometer was used to determine the interfacial angles of facets in the $[001]$ zone. A section perpendicular to the $[001]$ axis is shown in Fig. 3.16. The observed interfacial angles agreed with those calculated from the crystallographic data on the faces as shown in Fig. 3.16.

Damaged crystals also showed $\{100\}$ faces under goniometric inspection - these were subsequently found to be easily formed by cleavage. This and a similar cleavage perpendicular to the $[010]$ axis later proved invaluable in the specimen fabrication described in Chapter 4.

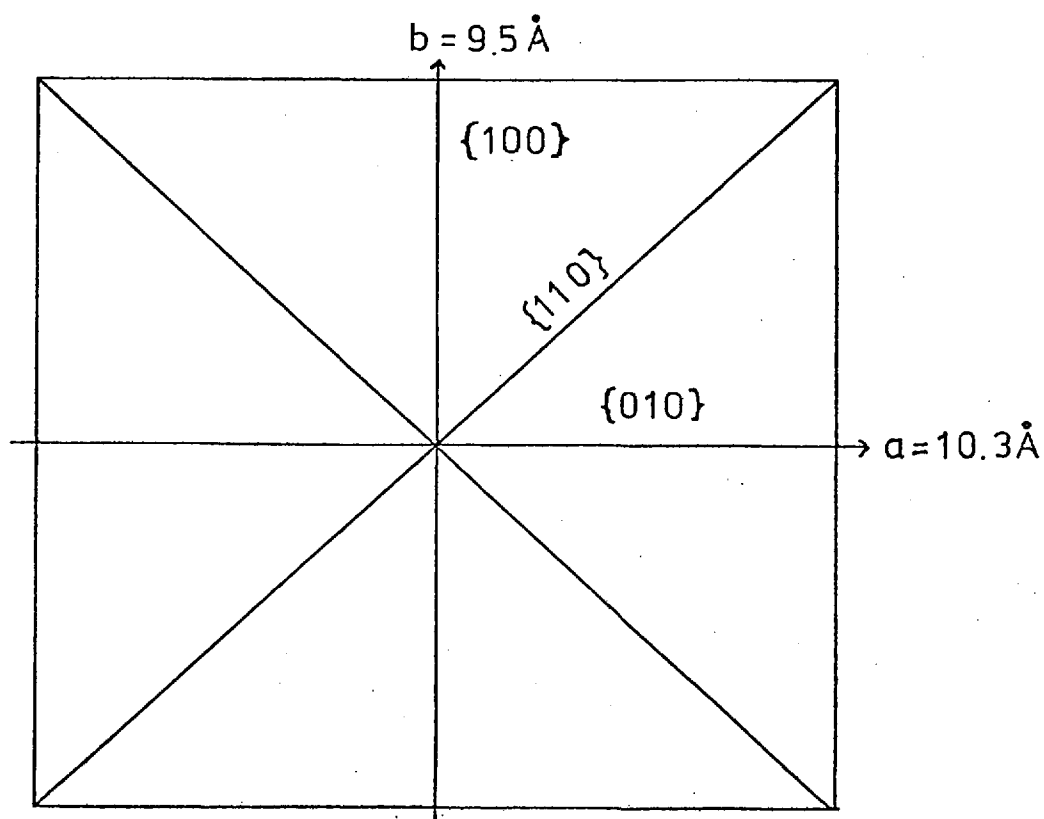
The most prominent feature of the morphology was the extremely 'polar' shape of the crystals. The (001) face was present, but too rough to give a clear reflection in the goniometer, while no other $\{hkl\}$ facets had formed. At the other end, however, the $\{111\}$ facets were dominant but gave way to an (001) facet of small area.

3.4. Discussion

A direct comparison may be made between the morphological observations and the results of the space group determination for FNPB reported in the last chapter. Sections of crystals perpendicular to



(a) Section of crystal perpendicular to $[001]$



(b) Section of lattice perpendicular to $[001]$

Fig.3.16 - Diagrams of the $[001]$ zone of FNEH

$[001]$ showed the expected mm symmetry, $\{010\}$ and $\{110\}$ facets being dominant with the $\{010\}$ faces having the largest area. The appearance of these facets is as predicted by the law of Donnay and Harker (1937), the lattice plane separation being largest perpendicular to the $[010]$ direction (9.5 Å) followed by that perpendicular to the $[110]$ direction (7.3 Å). The absence of a $\{100\}$ facet is due to the effective halving of the corresponding lattice plane separation by the presence of an a glide in the structure.

The agreement of the results with Donnay and Harker's law is in accordance with the theory of surface roughness described earlier (eqn. 3.4) - planes widely spaced in the lattice would be expected to have a higher degree of in-plane than out-of-plane bonding; thus these planes are stabilized and form facets.

The surface roughness treatment may only be successfully applied to the facets in the $[001]$ zone, in which the polar axis has no component in the growth direction. In other cases a marked difference was observed between $\{hkl\}$ and $\{hk\bar{l}\}$ facets. The growth on the $(00\bar{1})$ facet was anomalous, being sufficiently slow to prevent the formation of other $\{hk\bar{l}\}$ facets yet being of surprisingly poor quality - Fig. 3.17 shows a typical trail of inclusions formed during growth on the $(00\bar{1})$ face.

The slow rate and poor quality of growth on the $(00\bar{1})$ face both suggest that poisoning of the surface had occurred. Because of the point group symmetry, the (001) facet and all other facets not in the $[001]$ zone may possess a net surface charge. While in contact with a polar solvent such as methanol, this charge would immediately be neutralised by that of an adsorbed layer of ions or dipoles. As the sign of the initial charge is opposite at opposite ends of the crystal, the nature of the adsorbed layer would be different. It may be then assumed that the adsorbed layer on the (001) and $\{111\}$ faces are non-poisoning, or

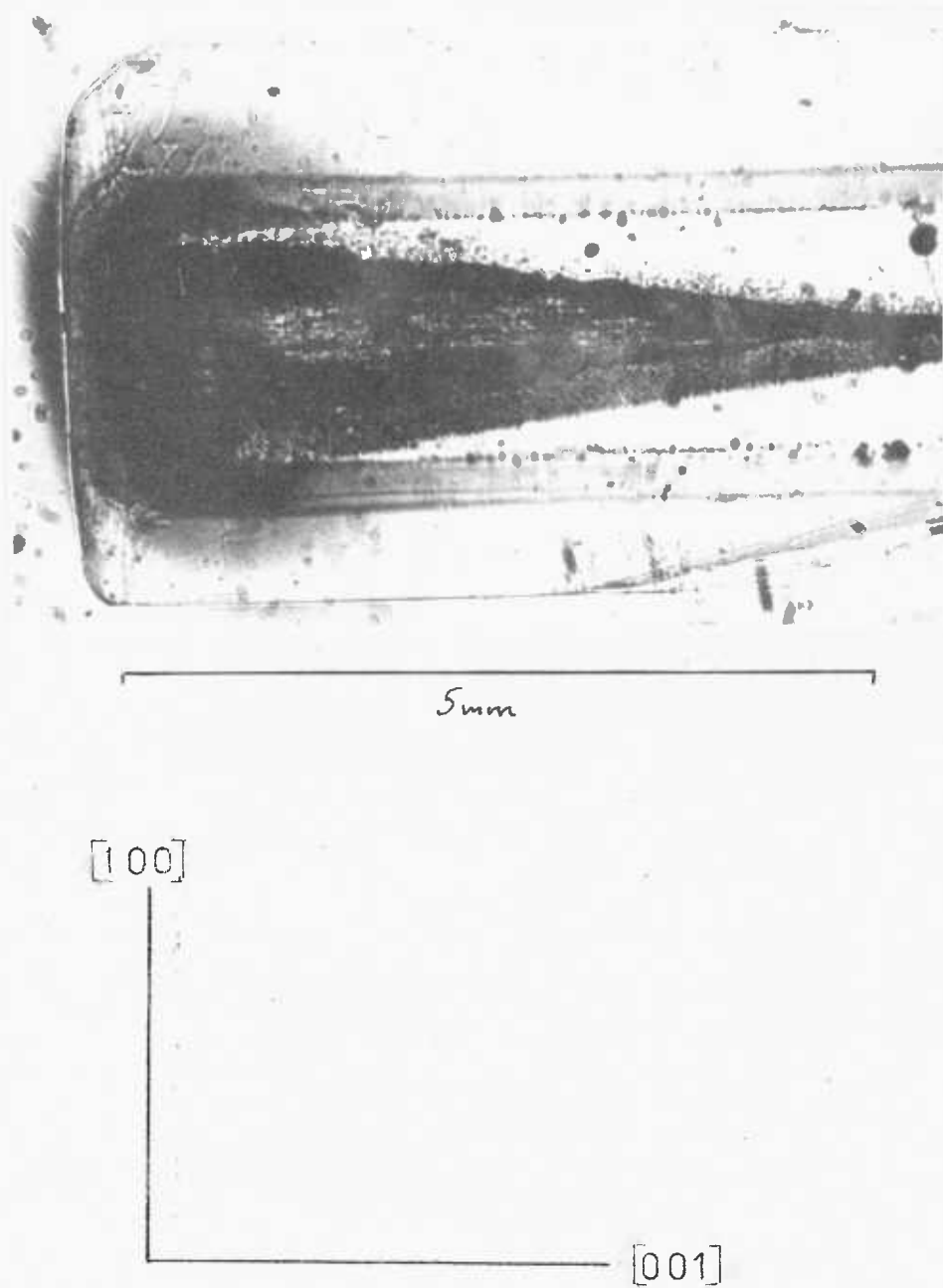


Fig. 3.17 - Photomicrograph of a crystal showing an inclusion trail behind the $(00\bar{1})$ face.

even beneficial to growth in facilitating the re-orientation of molecules during surface incorporation.

Compared with the rapid growth of small crystals in initial experiments, the results obtained under controlled conditions was disappointing. Although the rate of growth of large crystals was slower the quality of the crystals was not as good; these crystals showed inclusions and a tendency towards cracking, caused by strain, which were not present in the small crystals. Two reasons may be suggested for the deterioration during growth. First, decomposition of the solution, which was observed during the long growth cycle, was probably responsible for the poisoning of at least one facet. Although this may seem a formidable problem to overcome, remedies may be sought through addition of an antioxidant or other stabilizing agent and by a more efficient use of the limited lifetime of the solution by maintaining the maximum achievable growth rate throughout. A second possible reason for deterioration of growth is that the supersaturation was not constant during the long runs whereas in the short experiments any relatively small fluctuations of the high supersaturation were effectively damped by the diffusion barrier set up in the absence of stirring. A more accurate control of supersaturation is clearly required for successful growth of large crystals. This may be achieved by the application of a more accurately computed cooling programme to maintain steady growth, or by a solvent circulation method such as outlined in section 3.2. Another refinement in growth procedure would be to mount seeds on a flat seed holder so that the $(00\bar{1})$ face did not come into contact with the solution. Such a method is described for the growth of TGS (Weidmann (1972)).

In conclusion, it may be said that the above study of the growth of FNPB was successful in providing crystals suitable for electro-optic

measurements. Once suitable specimens had been obtained, work on crystal growth was terminated. Although the crystallisation proved more difficult than originally estimated, difficulties were of a practical rather than a fundamental nature. It is considered that if FNPH were required for electro-optic devices, crystals of sufficient size and quality would be at least as accessible as the current modulator materials, e.g. KD*P and lithium niobate.

CHAPTER 4 : THE ELECTRO-OPTIC PROPERTIES OF FNPH

Introduction

Crystals of two compounds, FNPH and 2MMNA, were grown to sufficient size and quality for electro-optic evaluation. However, owing to the absence of good cleavage planes in the crystals of 2MMNA, specimen fabrication of this material proved difficult, and within the time available an electro-optic evaluation could not be achieved for this material. This chapter describes the successful evaluation of some electro-optic constants of FNPH.

In addition to the electro-optic half-wave voltages, some data were collected on the absorption band structure and the refractive indices of FNPH. This was done for two reasons: the data are essential in any physical interpretation of the electro-optic half-wave voltages; also a knowledge of the absorptive and refractive properties would be required for the design of modulators incorporating FNPH.

4.1. Refractive Index Measurements

FNPH belongs to the orthorhombic crystallographic class and therefore is optically biaxial, having three principal refractive indices along the principal directions which lie along the crystallographic axes. The dielectric impermeability tensor, referred to the crystallographic axes, is then of the form:

$$(B_1, B_2, B_3, 0, 0, 0) \text{ where } B = \frac{1}{n^2}$$

Small, well-formed crystals similar to those used for the crystallographic experiments of Chapter 2 were used to determine the three refractive indices by the method of immersion. The experimental arrangement is shown

in Fig. 4.1(a). To determine n_a , the crystal was mounted on the stage with its (010) face perpendicular to the optical axis of the microscope, polarizer and analyzer set parallel to the crystallographic X axis. Various mixtures of α -bromonaphthalene and bromobenzene were placed in the cell, covering the crystal, until a mixture was found which exactly matched the crystal by the Becke Line method (Hartshorne and Stuart (1960)). The refractive index of the matching liquid at 589.3 nm was then found using an Abbe refractometer.

After adjusting the polarizer and analyzer to be parallel to the Z axis, n_c was found in the same way.

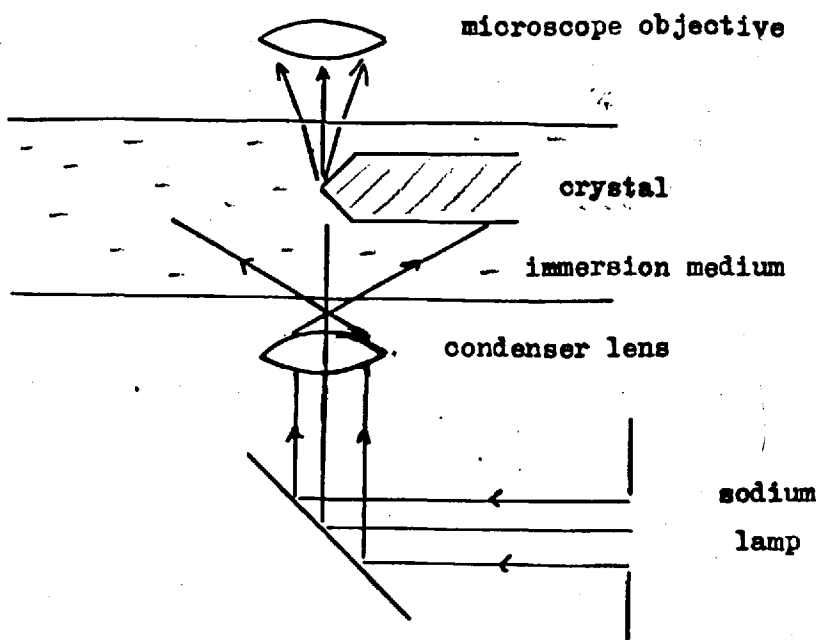
The values obtained were:

$$\underline{n_a = 1.64}$$

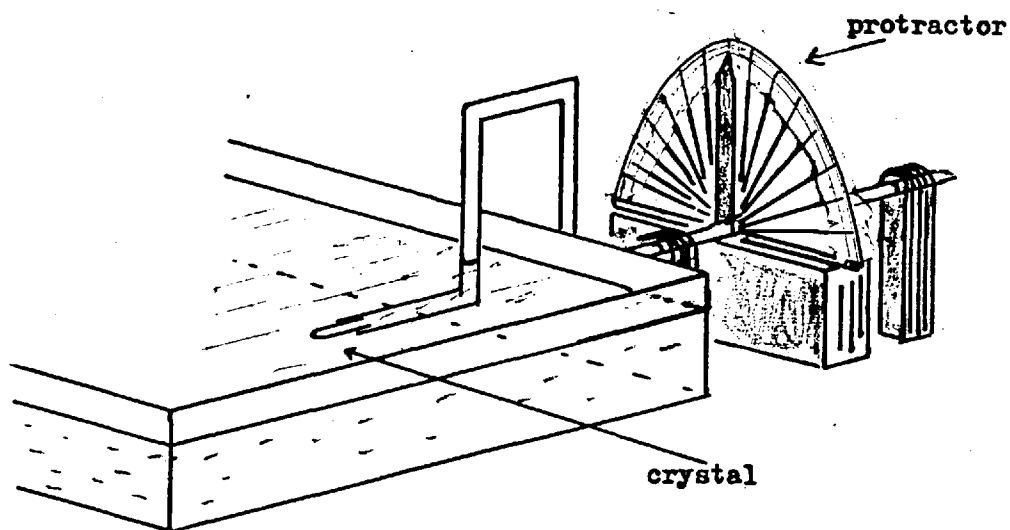
$$\underline{n_c = 1.60}$$

The crystal was then turned so that its X axis was parallel to the optical axis of the microscope. The previously determined value for n_c was confirmed, but n_b was found to be larger than the most optically dense medium applicable, i.e. methylene iodide, $n = 1.72$. (Some of the super-high refractive index mixtures listed in Hartshorne and Stuart were tried but found to react chemically with FNPH.)

The crystal was then mounted on a stage which allowed it to be partially rotated about its Z axis (Fig. 4.1(b)). The polarizer and analyzer were set perpendicular to the Z axis and the crystal was immersed in a mixture of methylene iodide and bromonaphthalene of refractive index 1.70. Starting with the Y axis vertical, the crystal was tilted about the Z axis until its refractive index appeared to match that of the liquid, and the angle of tilt was measured. The procedure was



(a) The method of immersion



(b) Apparatus for tilting the crystal

Fig.4.1 - Refractive index measurement

repeated, this time rotating about the X axis with the polarizer and analyzer set perpendicular to this axis. In Appendix II an expression for n_b in terms of a non-principal index n_β measured by the above method is given as:

$$n_b = \frac{n_\beta^2 - n_i^2 \cos^2 \theta}{\sin^2 \theta} \quad (A2.3)$$

where $i = a \text{ or } c$

$\theta =$ angle of tilt of X (or Z) axis from the horizontal.

Tilting about the Z axis, $n_\beta = 1.70$, $\theta = 26^\circ$, $n_a = 1.64 \quad \therefore n_b = 1.84$

Tilting about the X axis, $n_\beta = 1.70$, $\theta = 30^\circ$, $n_c = 1.60 \quad \therefore n_b = 1.96$

An average value was taken as $n_b = 1.9$

During the determinations of n_a and n_c , with the (010) plane lying horizontal, well defined birefringence fringes could be seen when the polars were crossed at 45° to the X axis; these are shown in Fig. 4.2. The fringes illustrate the optical retardation of eqn. 1.22:

$$\Gamma_o = \frac{2\pi\ell}{\lambda_o} (n_c - n_a) \quad (1.22)$$

A geometrical diagram of a section perpendicular to the Z axis is shown in Fig. 4.2, from which we may derive the relation between optical path length and horizontal distance along the wedge formed by the (110) faces:

If d is the fringe spacing

ℓ is the change in path length

θ is as shown

$$\frac{CD}{BD} = \tan \theta$$

$$\ell = 2CD = 2d \tan \theta$$

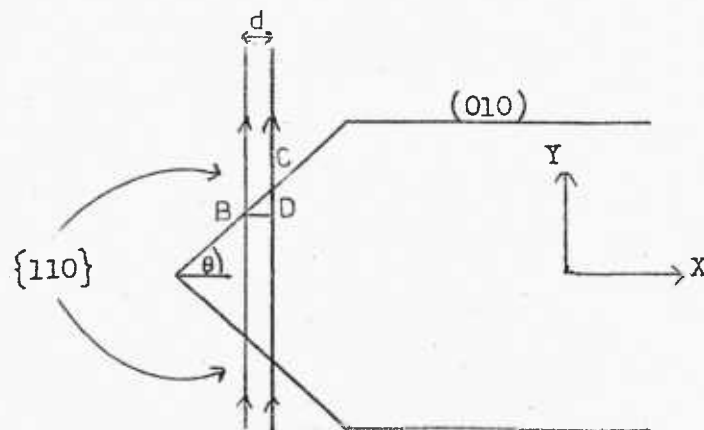
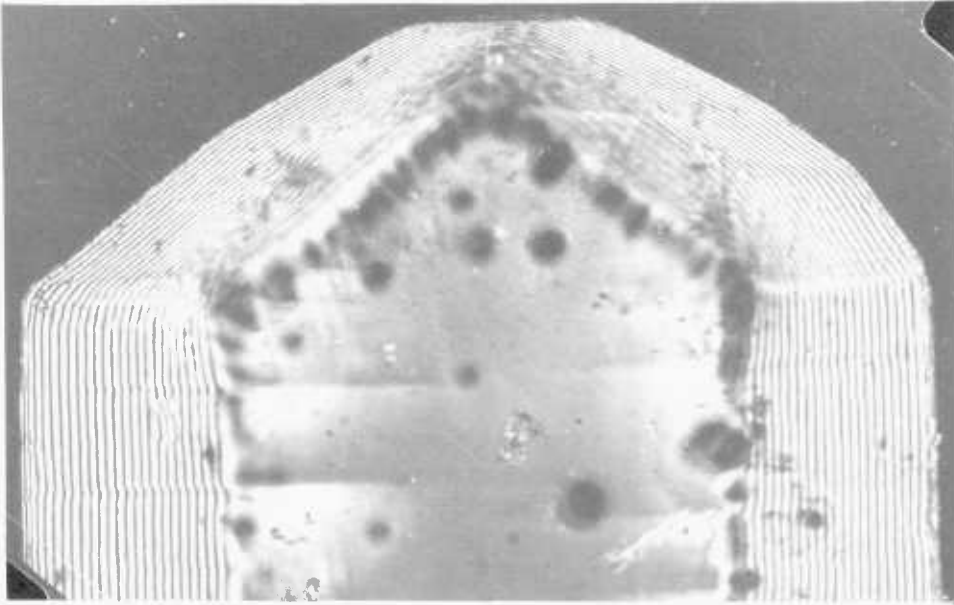


Fig. 4.2 - Photomicrograph and diagram showing the formation of birefringence fringes.

A change from one dark fringe to the next corresponds to a change in $\int_0$ of 2π , then from eqn. 1.22 we have

$$2\pi = \frac{2\pi}{\lambda} (n_c - n_a) 2d \tan \theta$$

$$n_c - n_a = \frac{\lambda}{2d \tan \theta} \quad (4.1)$$

The fringe spacing of Fig. 4.2 was measured and, using eqn. 4.1 an accurate value of $n_a - n_c$ was determined;

$$d = 6.00\mu$$

$$\theta = 42.0^\circ$$

$$\lambda = 0.5893\mu$$

$$\underline{n_a - n_c = 0.054}$$

4.2. The Linear Electro-optic Properties of FNPH

Introduction

Some half-wave voltages describing the electro-optic behaviour of FNPH were measured using the experimental arrangement shown simply in Fig. 4.3. The crystal specimen was positioned between crossed polarizing filters through which passed the laser beam. The light entering the specimen was polarized at 45° to the two privileged directions of the crystal so that it was resolved within into equal components polarised along these directions. Ideally, the transmission of the system should vary sinusoidally with the optical retardation between fast and slow rays in the crystal which, in turn, should be directly proportional to the applied field for a linear electro-optic effect.

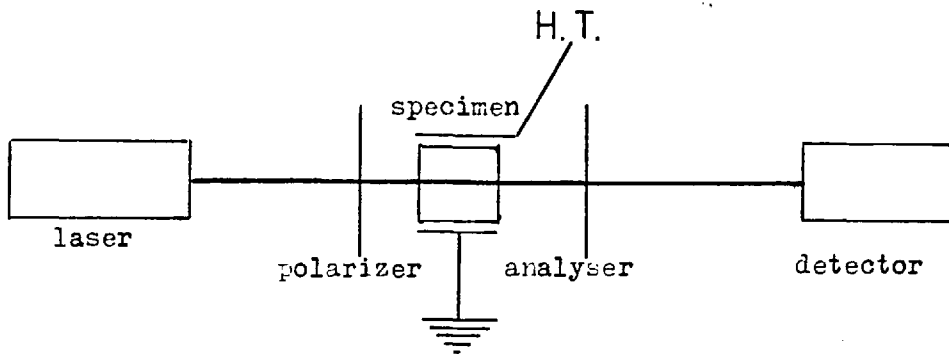
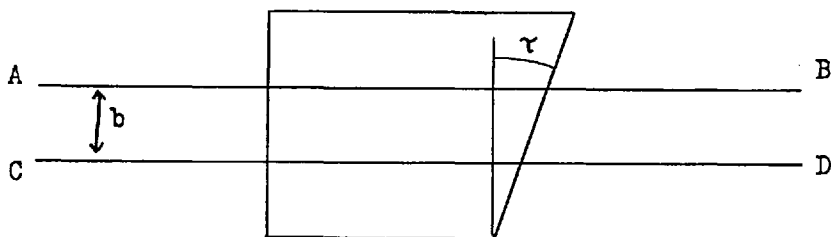


Fig.4.3 - Simplified diagram of electro-optic test



Difference in optical path lengths, $AB - CD = b.n.\tan \tau$

Fig.4.4 - The loss of phase definition due to non-parallel optical faces.

The half-wave voltage measured is a function of the light propagation and field directions; with the field applied along the polar axis, Z, and light propagated along the three principal axes respectively, half-wave voltages are as shown in Table 4.1.

Light propagation direction	Field direction Z		
	X	Y	Z
V	$\lambda_o d / (n_2^3 r_{23} - n_3^3 r_{33})$	$\lambda_o d / (n_1^3 r_{13} - n_3^3 r_{33})$	$\lambda_o d / (n_1^3 r_{13} - n_2^3 r_{23})$
mode	transverse	transverse	longitudinal

Table 4.1

The last half-wave voltage tabulated represents the longitudinal effect, in which the light passes through the field electrodes. This arrangement is experimentally inconvenient and since the result is not independent of the two transverse half-wave voltages a direct measurement of the longitudinal effect was not attempted. The following is an account of the measurement of the transverse half-wave voltages.

4.2.1. Fabrication of Specimens

A successful electro-optic birefringence measurement is subject to the following conditions:-

- (1) that the beam may enter, pass through and emerge from the specimen without excessive deviation or scattering;
- (2) that the phase retardation between the two plane polarized components of the light traversing the specimen is constant throughout the beam cross-section.

The first condition requires the optical faces of the specimen to

be parallel, perpendicular to the beam and optically flat compared with the wavelength of the light. Also the crystal section must be chosen to be free from cracks or other defects capable of scattering the beam.

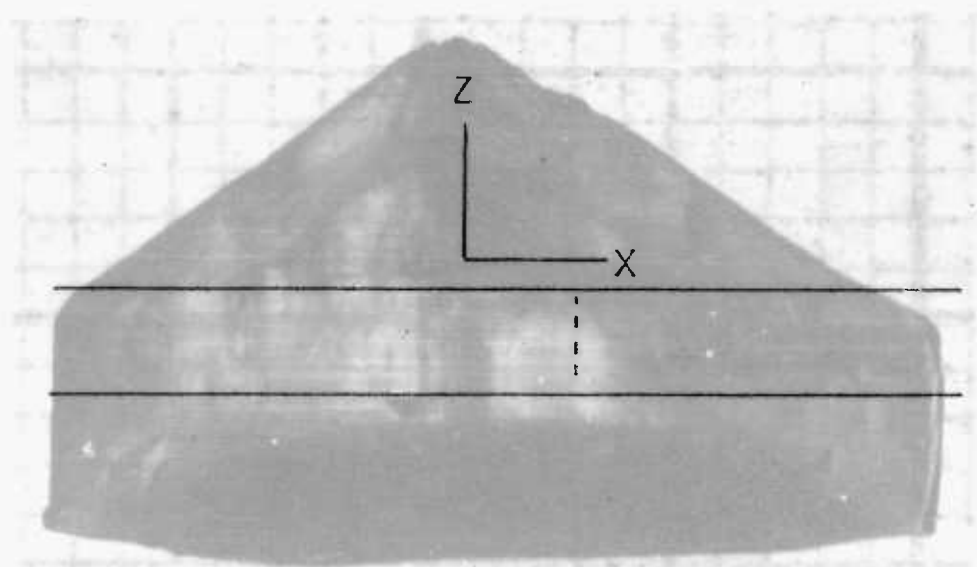
The second condition indicates that the strain birefringence of the crystal must be small and defines a maximum allowed deviation from parallelism of the faces. With reference to Fig. 4.4 the angle between the faces, τ , must be such that

$$b(n_3 - n_2) \tan \tau \ll \lambda_0$$

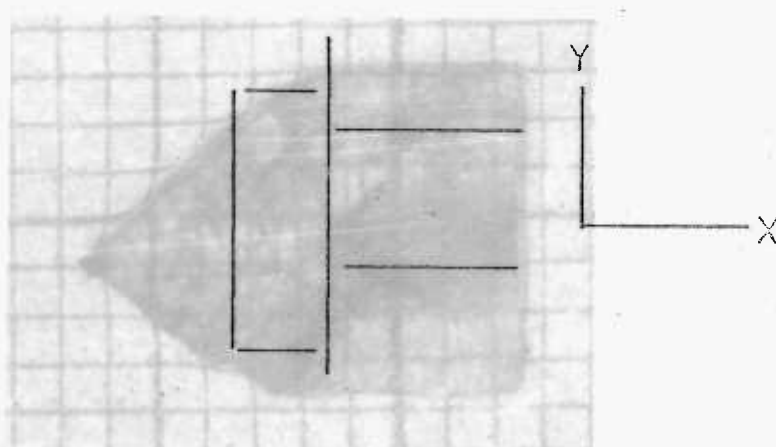
Fig. 4.5 shows the stages in cutting a crystal into oriented cuboids. After examination of the crystal for uniform extinction between crossed polars, the first cuts, perpendicular to the Z axis, were made with a wet string cutter using industrial ethanol as the solvent. The resulting slice was then labelled with the polarity of the Z axis and cleaved perpendicular to the X and Y axes respectively, using a sharp razor blade.

(In the manufacture of electro-optic modulators it is usual to employ a crystal with a large aspect ratio, i.e. a large ratio of light path to interelectrode spacing, so that half-wave retardation is achieved on the application of a fraction of the half-wave voltage of the material. In this case, however, the poor quality of the crystals available made the avoidance of imperfections difficult over long light paths. A relatively long interelectrode distance was not considered a disadvantage under laboratory conditions since the maximum electro-optic retardation attainable was limited by the dielectric breakdown field rather than the available supply voltage.)

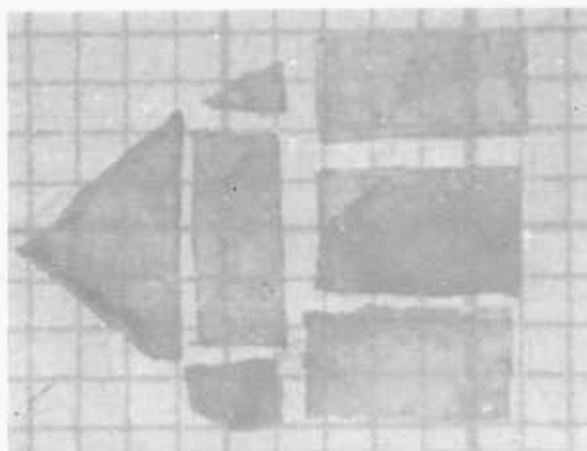
Considerable difficulty was encountered in attempts to polish the optical faces. This was due to the smallness and fragility of the

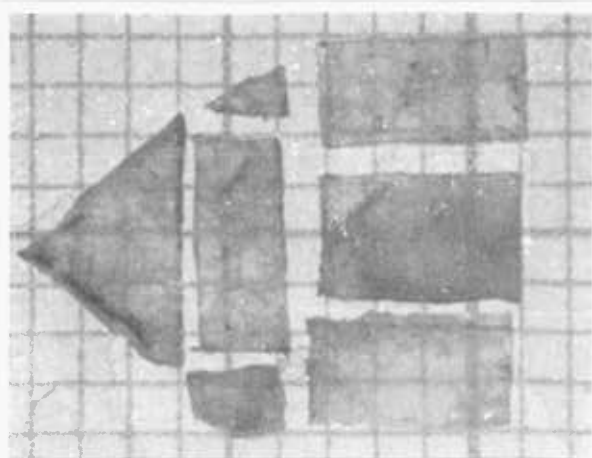
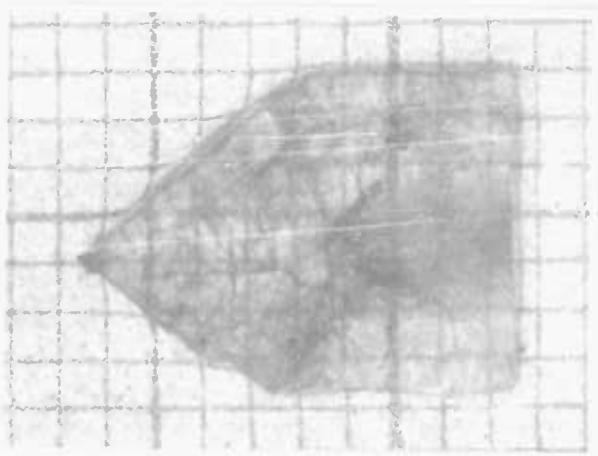
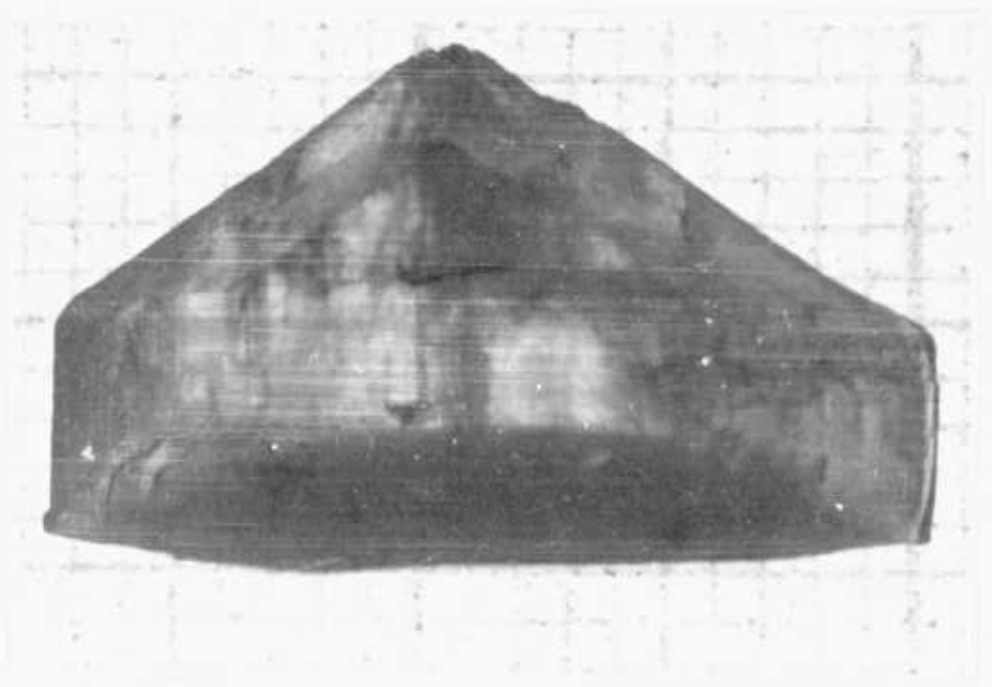


(a) Wet string cutting of a Z plate.



(b) Cleavage along (100) and (010) planes.





specimens which made handling difficult, and to the lack of suitable adhesives or encapsulants for rigid mounting. Thermal and strains inevitably introduced in the polishing process invariably caused cracks to appear in clear regions.

Unpolished, cleaved surfaces were microscopically examined and found to have optically flat areas of up to 0.5 mm in diameter which were connected by steps of a few microns. The flat areas were all parallel to each other, being (010) and (100) faces, and therefore beams of small diameter could pass through the crystal without loss of coherence. For the electro-optic measurements, the laser beam was brought to a focus at the centre of the specimen, as shown in Fig. 4.6. The focussing has a slightly detrimental effect on the coherence of the emerging beam, but the following calculation justified the validity of the results.

The geometrical path difference between axial ray and ray furthest from axis is:

$$\begin{aligned} AD - BC &= \sqrt{d^2 + \ell^2} - \ell \\ &\approx \frac{d^2}{2\ell} \end{aligned}$$

$$\text{then } \Gamma_{AD} - \Gamma_{BC} = \frac{2\pi}{\lambda} \Delta n \frac{d^2}{2\ell}$$

$$\text{for } \Delta n = 0.3, \lambda_0 = 632.8 \text{ nm}, d \approx 10^{-3} \text{ cm}, \ell = 0.25 \text{ cm}$$

$$\Delta \Gamma = \frac{\pi}{50}$$

Prior to electro-optic evaluation, the aspect ratio of each specimen was measured using a micrometer then the faces perpendicular to the Z axis were completely coated with silver dag. The (00 $\bar{1}$) face of the specimen was then attached to a cover glass painted with silver dag and a thin copper wire was connected to the (001) face also with silver dag.

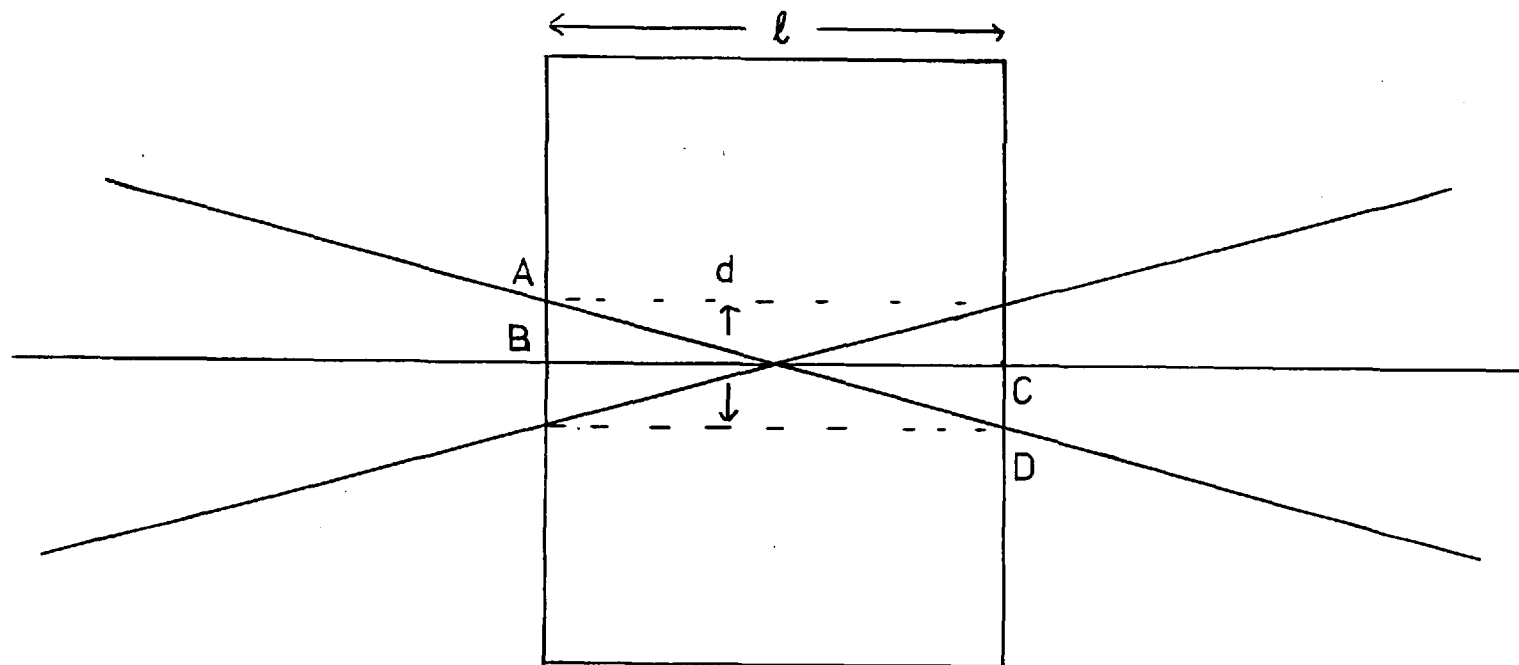


Fig.4.6 - Focussed beam passing through the sample (see text).

4.2.2. D.C. Electro-optic Birefringence Measurements

The optical bench was set up as shown in Fig. 4.7. The condenser lens ($f = 10$ cm) focussed the 0.5 mm diameter beam to a spot $\sim 10\mu$ diameter at the incident face of the crystal. The emergent beam was projected by the second lens to give a real image of the crystal with 3x magnification at the focus of the microscope. (Special care was taken to estimate the beam intensity and attenuate it accordingly before looking down the eyepiece.) By suitable adjustments of the goniometer stage several areas of the crystal were found which allowed the beam to pass through undeviated, the beam also showing good extinction as the quartz wedge was adjusted. One such area was chosen then the microscope was replaced by a photo-diode (Mullard BPY13) so that the resultant intensity could be monitored with a Keithley electrometer.

The photo-diode current (I) was monitored while the quartz wedge position (x) was adjusted over a range of 5 cm in 0.05 cm steps; a typical result is plotted in Fig. 4.8(a).

Referring to this graph the wedge was set at A, the centre of the almost linear part of the sinusoidal $I - x$ curve. The change in photo-diode current was then measured as a function of applied voltage (Fig. 4.8(b)). Readings of current vs voltage were again taken with the wedge set at B (Fig. 4.8(c)).

The photo-diode current may be written:

$$\begin{aligned}
 I &= I_{\min} + \frac{I_0}{2} (1 - \cos \Gamma) \\
 \frac{dI}{d\Gamma_e} &= \frac{I_0}{2} \sin \Gamma_0 \\
 &= \frac{I_0}{2} \quad \text{when } \Gamma_0 = \frac{\pi}{2} \\
 &= -\frac{I_0}{2} \quad \text{when } \Gamma_0 = \frac{3\pi}{2}
 \end{aligned}$$

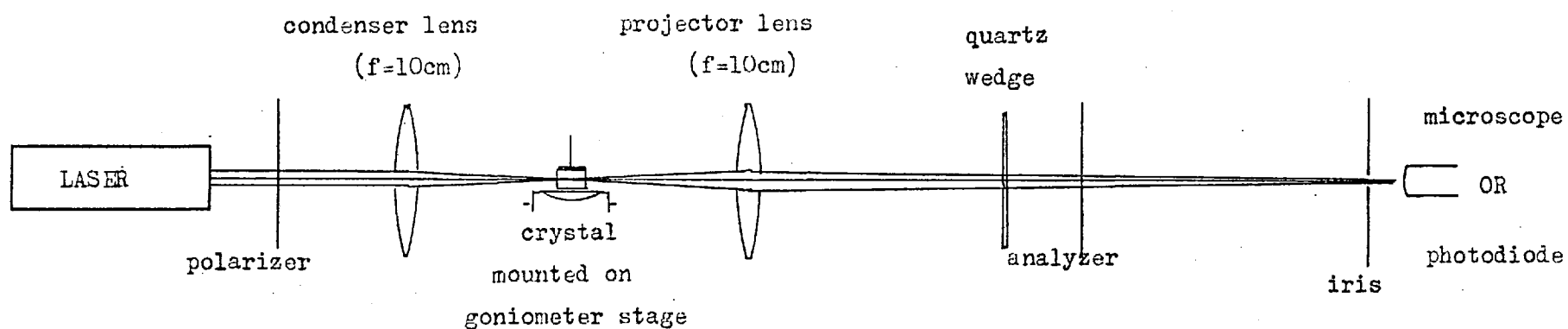
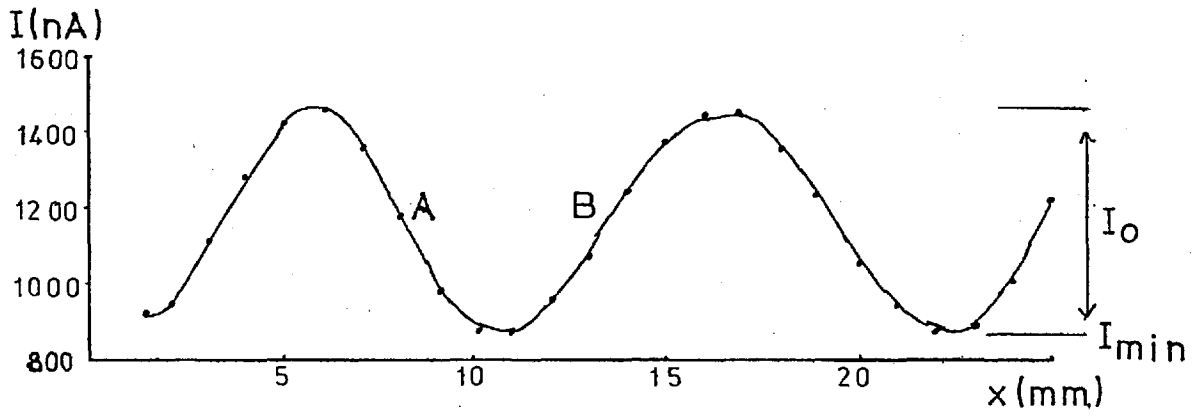
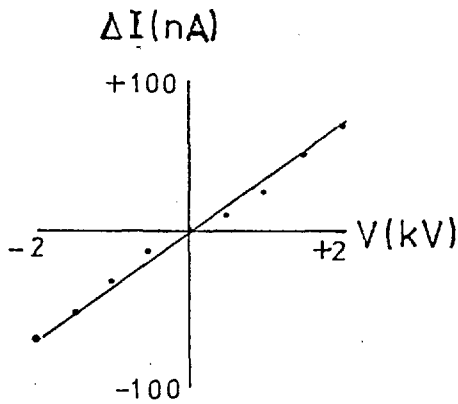


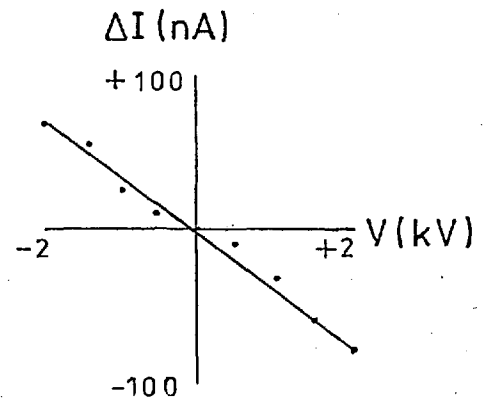
Fig. 4.7 - Experimental arrangement for D.C. electro-optic evaluation.



(a) Variation of photo-diode current with wedge position.



(b) Current vs voltage with wedge in position A.



(c) Current vs voltage with wedge in position B.

Fig.4.8 - Typical results of electro-optic evaluation.

$$\begin{aligned}
 \text{then } \frac{d\Gamma_e}{dV} &= \frac{dI}{dV} \bigg/ \frac{dI}{d\Gamma} \\
 &= \frac{2}{I_o} \frac{dI}{dV} \text{ for } \Gamma_o = \frac{\pi}{2} \\
 &= -\frac{2}{I_o} \frac{dI}{dV} \text{ for } \Gamma_o = \frac{3\pi}{2}
 \end{aligned}$$

$$V = \Gamma_e \frac{dV}{d\Gamma_e}$$

$$V_{\lambda/2} = \pi \frac{dV}{d\Gamma_e} = \pm \frac{I_o}{2} \pi \bigg/ \frac{dI}{dV}$$

where $I_{\min}$ is the background current from depolarised light

$$I_o = I_{\max} - I_{\min} \text{ (see Fig. 4.6(a))}$$

$$\Gamma_o = \text{optical retardation}$$

$$\Gamma_e = \text{electro-optical retardation}$$

$$\Gamma = \Gamma_o + \Gamma_e$$

$$V = \text{applied voltage.}$$

Results

(1) Light Propagated along X

$$V_{\lambda/2} = 27 \text{ kV, } \ell = 1.63 \text{ mm}$$

$$d = 2.76 \text{ mm}$$

$$\therefore V_{\lambda/2} = 16 \text{ kV for the material.}$$

The effect of a positive voltage corresponded to an increase in quartz wedge thickness. This amounts to greater retardation along the slow axis of the wedge, corresponding to the Y axis of the FNPH sample. Then, by the notation of Chapter 1:

$$\frac{V_{\lambda/2}^{Y-Z}}{} = + 16 \text{ kV}; \quad n_3^3 r_{33} - n_2^3 r_{32} = + 4.0 \times 10^{-11} \text{ mV}^{-1}$$

at $\lambda = 632.8 \text{ nm}$

(2) Light propagated along Y

$$\frac{V_{\lambda/2}}{} \simeq 40 \text{ kV} \quad \ell = 1.79 \text{ nm} \quad d = 2.42 \text{ nm}$$

$$\frac{V_{\lambda/2}}{} \simeq 30 \text{ kV for the material}$$

Again a positive voltage gave the same effect as increasing wedge thickness,

$$\therefore \frac{V_{\lambda/2}^{X-Z}}{} = + 30 \text{ kV}; \quad n_3^3 r_{33} - n_1^3 r_{31} = + 2.1 \times 10^{-11} \text{ mV}^{-1}$$

4.2.3. High Frequency Modulation Experiments

Having established by the d.c. measurements that FNPH exhibited a sizeable electro-optic effect, the natural conclusion to this project was an investigation of the properties of FNPH as an optical modulator. Although the theoretical discussion in Chapter 1 predicts a possibility of modulation at frequencies well into the microwave range, a demonstration of such effects was outside the scope of this work. However, a suitable apparatus was available for studies at 1 MHz and the results are reported here.

Fig. 4.9 shows the additional equipment necessary for modulation experiments. An alternating voltage signal was applied to the crystal and the laser beam intensity monitored by a PIN diode, whose current output was amplified to give a voltage signal for display on the oscilloscope. This apparatus was considerably more sensitive than its D.C. equivalent but suffered the disadvantage that an absolute calibration would have been difficult; for this reason a longitudinal mode

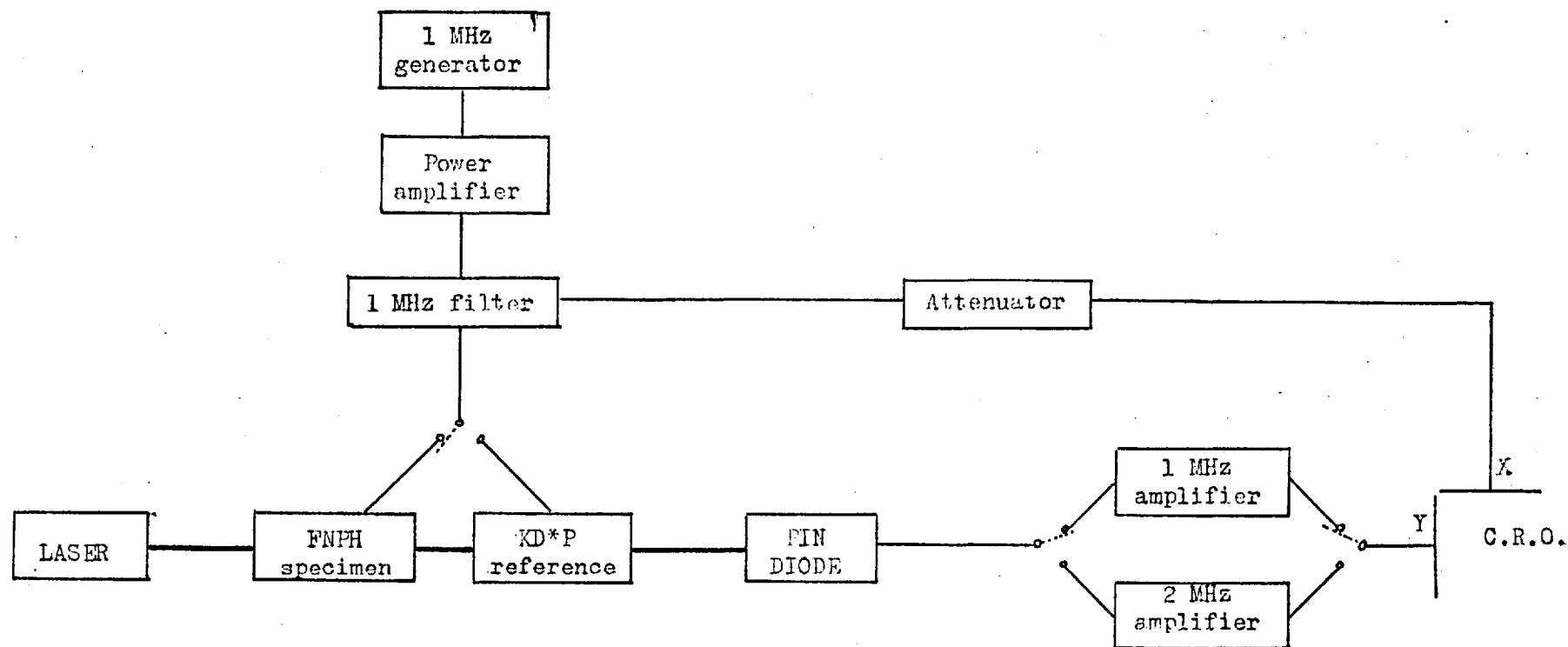


Fig. 4.9 - Block diagram of high-frequency modulation apparatus.

KD*P modulator was introduced as a reference. The reference cell and the sample were used in optical series for all measurements, so that the same effects of absorption and scattering were present each time.

Preliminary to the observation of modulation, the optical system was carefully aligned, and the various stages of electronic equipment tuned to match the power amplifier. Having done this, the position of the crystal was adjusted as in the D.C. measurements, this time using the oscilloscope display instead of the microscope to point out optically clear sections. A preliminary investigation showed that there were many areas of the crystal which gave large modulation signals. For each of these areas the quartz wedge was adjusted to verify the expected sinusoidal variation of modulation depth with optical retardation. The second harmonic, at 2MHz was seen to reach maxima and minima corresponding to the minima and maxima of fundamental modulation signal. The observations are in agreement with those expected of a linear electro-optic effect (cf. eqn. 1.26).

Measurements of the half-wave voltages were made by comparing the maximum output signal at 1MHz when the power was applied to the FNPH with the output when the same voltage was applied to the modulator. To avoid false readings, considerable care was taken to tune all the circuits to give the maximum output before taking a reading. Also the quartz wedge had to be adjusted each time the power was applied to the FNPH to allow for a rather large temperature coefficient in the birefringence, which manifested itself as approximately quarter-wave retardation appearing during the first few seconds after switching on the power.

It was found that for a given driving voltage, typically 700 V peak, the signals obtained from two FNPH specimens were as follows, compared with the KD*P modulator:

$$S_{KD*P} = 1$$

$$S_{FNPH} = 0.20 \quad (\text{light propagated along X})$$

$$S_{FNPH} = 0.25 \quad (\text{light propagated along Y})$$

The half wave voltage of the KD*P modulator was found to be 4.0 kV by a d.c. measurement, so that

$$V_{\lambda/2}^{Y-Z} = 20 \text{ kV}$$

and $V_{\lambda/2}^{X-Z} = 16 \text{ kV}$

Correcting these values using the aspect ratios as was done in the d.c. measurement, we have,

$$V_{\lambda/2}^{Y-Z} = 12 \text{ kV}; \quad n_3^3 r_{33} - n_2^3 r_{32} = 5 \times 10^{-11} \text{ mV}^{-1}$$

$$V_{\lambda/2}^{X-Z} = 12 \text{ kV}; \quad n_3^3 r_{33} - n_1^3 r_{31} = 5 \times 10^{-11} \text{ mV}^{-1}$$

4.3. The Infrared Spectrum of FNPH

FNPH crystals were ground as finely as possible in an agate mortar and a small quantity of the powder spread thinly between two sodium chloride plates. A Perkin-Elmer 357 spectrometer was used to draw the spectrum shown in Fig. 4.10.

The spectra of 4-nitrophenylhydrazine (NPH) and formamide (F) were found in spectral atlases (Grasseli (1973), Pouchert (1970)) and the main bands of these compounds are superimposed on the FNPH spectrum. Tentative assignments of some of the bands were made with reference to Bellamy (1958). Some C-H bands were expected near 3000 cm^{-1} , but these have been obscured, presumably by scattering of the incident beam by particles comparable in size to its wavelength. Otherwise, the spectrum shows the expected similarity to the 4-nitrophenylhydrazine and formamide spectra.

4.4. The Ultraviolet Spectrum of FNPH

The spectrum shown in Fig. 4.11 was drawn by a Perkin-Elmer 407 spectrometer, using a solution of FNPH in ethanol of concentration 10 mg l^{-1} supported in a silica cell. The three bands have wavelengths and approximate extinction coefficients as follows:

λ (nm)	ϵ_{max}
205	0.8×10^4
225	1.0×10^4
347	1.6×10^4

When viewed under a polarizing microscope, crystals of FNPH showed a deep yellow colour in transmitted light polarized parallel to the crystallographic Y axis, but only a pale yellow colouration in X or Z

axis polarized light. Further discussion of the spectrum and the associated dichroism will appear in the next chapter.

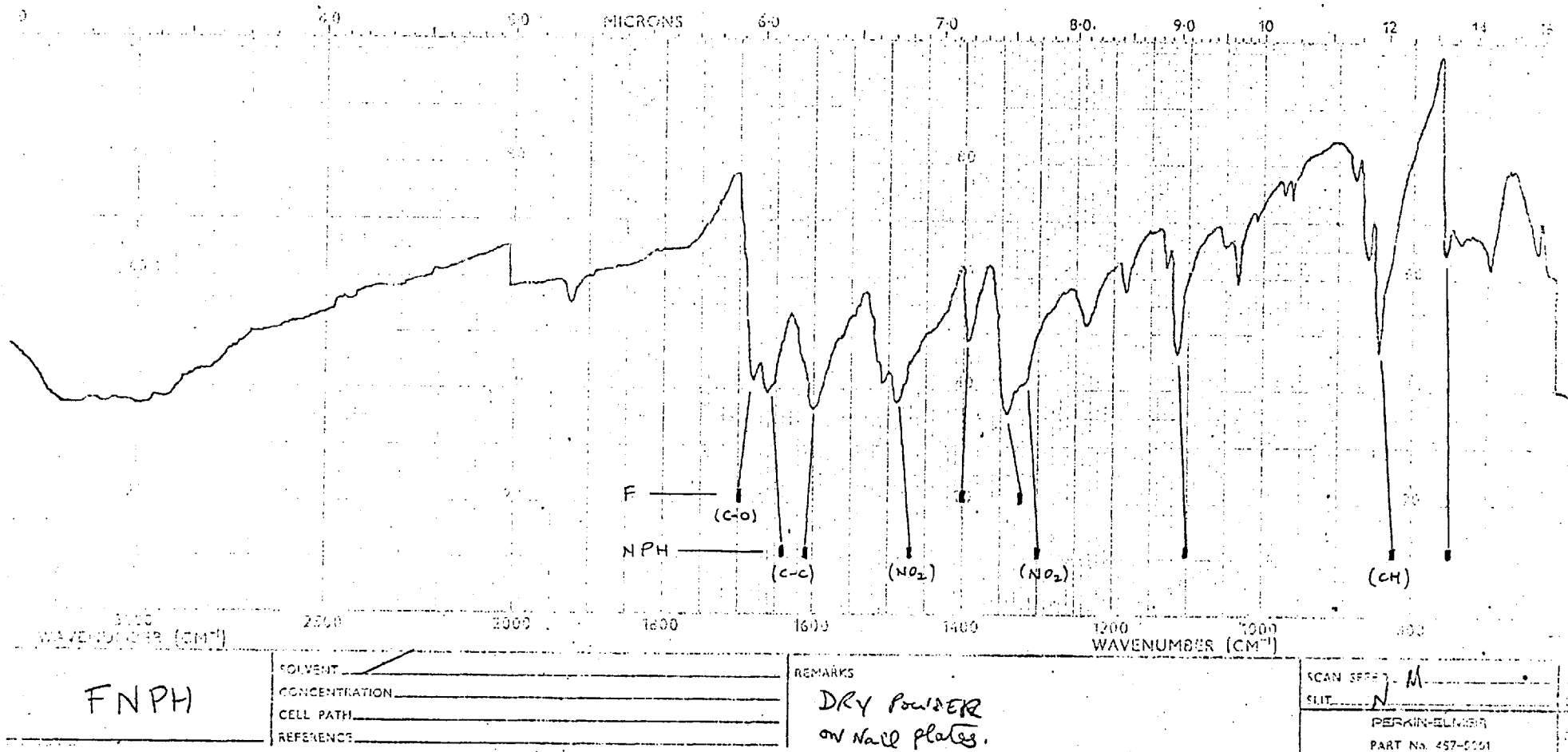


Fig. 4.10 - The infra-red spectrum of FNPH.

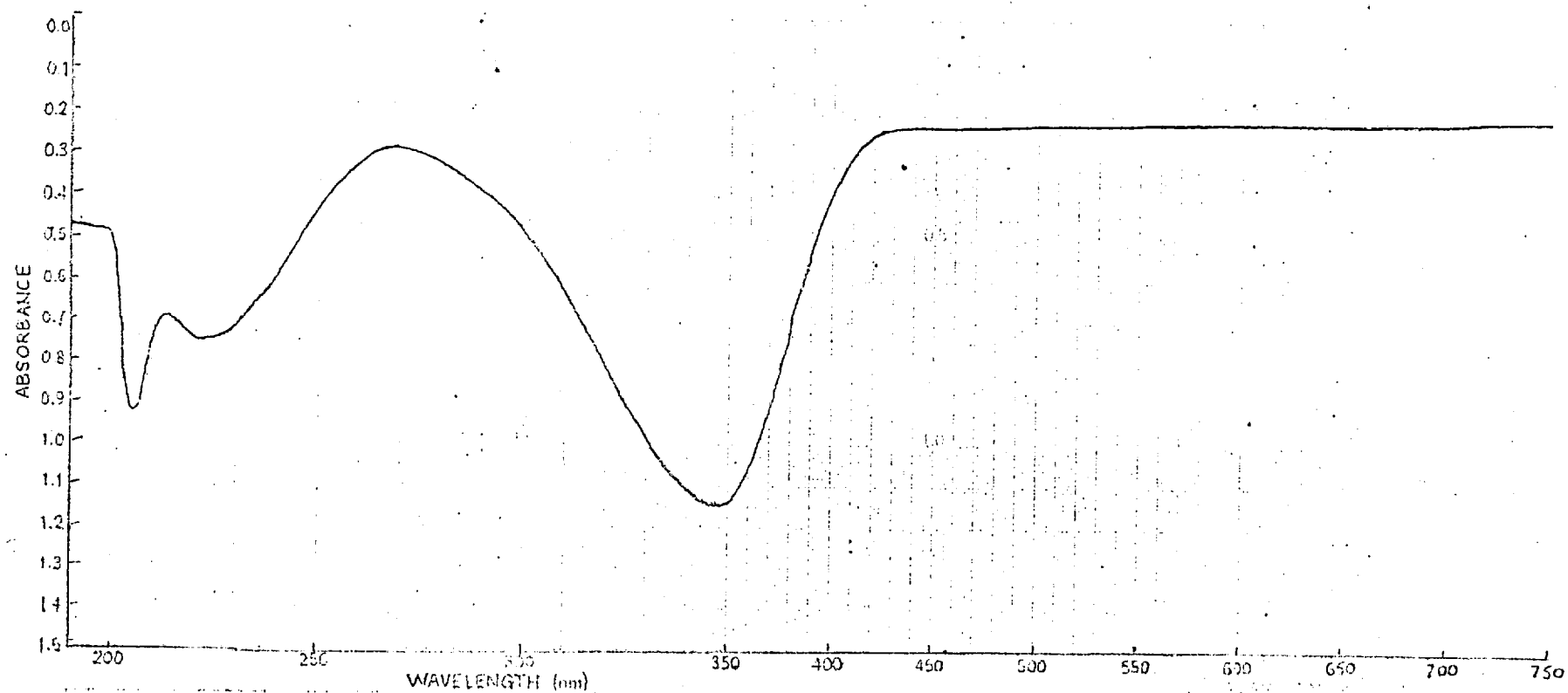


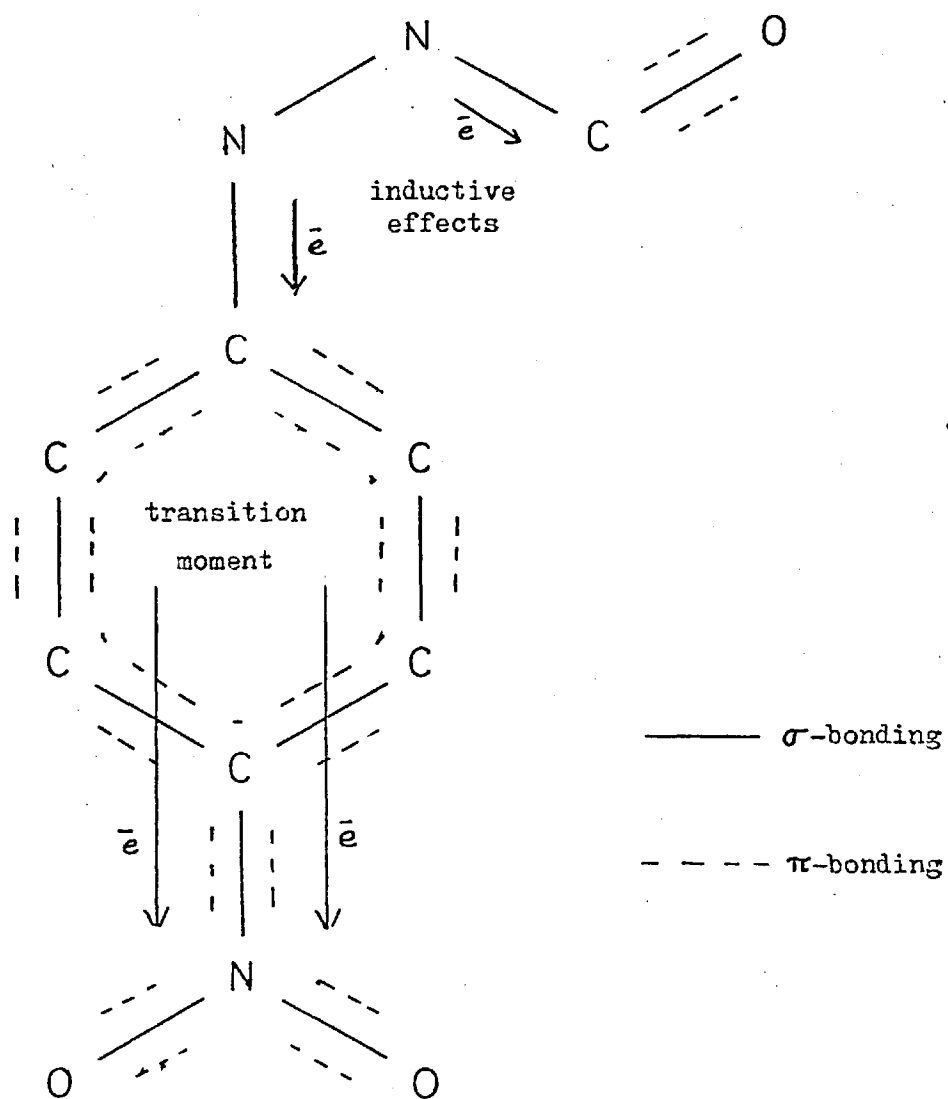
Fig. 4.11 - The ultra-violet and visible spectrum of FNPB.

CHAPTER 5 - DISCUSSION

This penultimate chapter presents an analysis of the optical properties of FNPH, which supplements the limited structure information available to give a clearer understanding of the molecular positions in the solid. The electro-optic and other non-linear phenomena are then interpreted in terms of the proposed crystal structure, and finally the implications of this work in the general field of organic electro-optic materials are discussed.

5.1. The Ultraviolet to Visible Spectrum of FNPH

The optical properties of FNPH in the near-visible range are dominated by a group of absorption bands in the ultraviolet spectrum, which were found to be at 205 nm, 225 nm and 347 nm respectively. The last band, at 347 nm is the largest, nearest to the visible range, and therefore has the greatest influence over the visible properties. This band corresponds to a similar band reported at 384 nm in 4-nitrophenylhydrazine (NPH) (Grasseli (1973)) and at 370 nm in 4-nitroaniline (PNA) (Tanaka (1963)). The 370 nm band in PNA has been attributed to the first charge transfer excited state formed from the nitro group to the aromatic ring (Godfrey and Murrell (1963)). This excited state is stabilized in PNA by the presence of the amino group. The same assignment is here assumed to apply to NPH, where the hydrazide group confers even greater stability, and to FNPH, where the formylhydrazide group confers less stability than the amino group to the excited state. The charge transfer is illustrated in Fig. 5.1. The two higher energy bands of FNPH, at 205 nm and 225 nm contrast with a single band at 230 nm in NPH; the extra band at 205 nm probably originates from the carbonyl group (cf. formamide which has a single



(Hydrogen atoms have been omitted for clarity.)

Fig.5.1 - The charge transfer transition of FNPB.

band at 205 nm (Grasseli (1973)).

The yellow colour of FNPH is entirely due to the tail of the 347 nm band. In the crystal, a large dichroism was visually observed: under transmitted polarized light the absorption was much larger for light polarized parallel to the b-axis; light polarized along a and c suffered little absorption. This observation implies that the molecules are oriented so that the direction of the transition, as indicated in Fig. 5.1, is mainly along the b-axis of the crystal.

5.2. The Crystal Structure of FNPH

For any discussion of the mechanism of the electro-optic effect and other effects of the non-linear polarization, some knowledge of the crystal structure is essential. X-ray diffraction work enabled the unit cell dimensions and symmetry to be determined, but these measurements alone give little insight into the positions and orientations within the cell.

The relative absorption of light polarized parallel to the respective crystal axes can provide accurate information about the molecular orientations. A classical treatment of absorption gives the absorption coefficients as proportional to the oscillator strengths, f_i , in each direction. The semi-classical treatments show that the oscillator strength corresponds to a function of the square of the transition moment length (Elliott (1974)). By resolving the square of the transition moment length along the crystal axes, the anisotropy may then be calculated. Such a calculation for 4-nitroaniline gave excellent agreement between the observed dichroic ratios and the crystal structure (Tanaka (1963)). Unfortunately, in the case of FNPH, the molecular orientations could not be established because of the qualitative nature of the absorption data.

Quantitative information was, however, collected for the principal refractive indices of FNPH:

$$n_a = 1.64$$

$$n_b = 1.9$$

$$n_c = 1.60$$

These results become more meaningful when converted into the respective Lorenz-Lorentz molar refractivities:

$$R = \frac{\bar{n}^2 - 1}{\bar{n}^2 + 2} \frac{M}{\rho} = \sum \frac{Bf_i}{\omega_o^2 - \omega^2} = \sum R_i \quad (5.1)$$

(cf. eqn. 1.7)

$$\text{where } \bar{n} = (n_a n_b n_c)^{1/3}$$

M = molecular weight

ρ = density

R_i = component refractivities ($i = a, b, c$).

The molar refractivity is a useful parameter because it may be split into additive components due to the atomic refractivities of each atom in the molecule and the refractivity contributions of various electronic transitions. Furthermore, the mean, three-dimensional refractivity may be divided into three orthogonal one-dimensional refractivities:

$$R = R_a + R_b + R_c \quad \text{where } R_i = \frac{1}{3} \frac{(n_i^2 - 1)}{(n_i^2 + 2)} \frac{M}{\rho} \quad (5.2)$$

Thus we may calculate the refractivities of FNPH as:

$$R = 46.14$$

$$R_a = 14.21$$

$$R_b = 18.34$$

$$R_c = 13.49$$

(The slight discrepancy in the sum arises from the use of a geometric mean instead of the true mean refractive index as defined by the Lorenz-Lorentz formula.)

Corresponding values for PNA are (Tanaka (1963))

$n_x = 1.556$	$R = 39.89$	$X \perp^r (101)$
$n_y = 1.777$	$R_x = 10.29$	$Y \parallel^r b$
$n_z = 2.005$	$R_y = 13.39$	$Z \perp^r X \perp^r Y$
	$R_z = 16.06$	

An approximate value of R^{CT} for the charge transfer transition may now be obtained from the knowledge that, in PNA, the oscillator strength due to the similar charge transfer has a zero component along the X axis, and a component along the Z axis of 80% of its maximum value:

$$R^{CT} = \frac{5}{4} (R_z - R_x) = 7.21 \quad (5.3)$$

This value of R^{CT} may be used to interpret the anisotropy in the refractivities of FNPH. To fit the data, R^{CT} would have to be distributed between the principal axes in the ratio $a:b:c = 0.18 : 0.74 : 0.07$. The direction cosines of the transition moment vector are therefore:

$$\cos \alpha = 0.18$$

$$\cos \beta = 0.74$$

$$\cos \gamma = 0.07$$

It has already been stated that the carbonyl group is expected to depress the charge transfer activity through its inductive effect, so the value of R^{CT} used above is probably too high for FNPH. If this were true the calculated anisotropy of the transition would be greater. Another value of R^{CT} may be obtained by an examination of the mean refractivity of FNPH, which may be calculated from the refractivities of constituent groups,

$$\begin{aligned} R(\text{FNPH}) &= R(\text{PNA}) + R(\text{Formamide}) - 2R(\text{Hydrogen}) & (5.4) \\ &= 39.89 + 10.65 - 2.20 \\ &= 48.34 \end{aligned}$$

($R(\text{Formamide})$ was calculated from the refractive index (Weast (1973)) and $R(\text{Hydrogen})$ is given in Partington (1953)).

Comparison with the experimental value shows a reduction of R^{CT} by 2.20. However, the reduced value of 5.01 for R^{CT} in FNPH is not large enough to explain the observed anisotropy in R . The true value of R^{CT} must therefore be taken as between 5.01 and 7.21.

To summarize the above argument, an examination of the refractive indices gave estimations of the direction cosines of the transition vector as:

$$\cos \alpha < 0.07$$

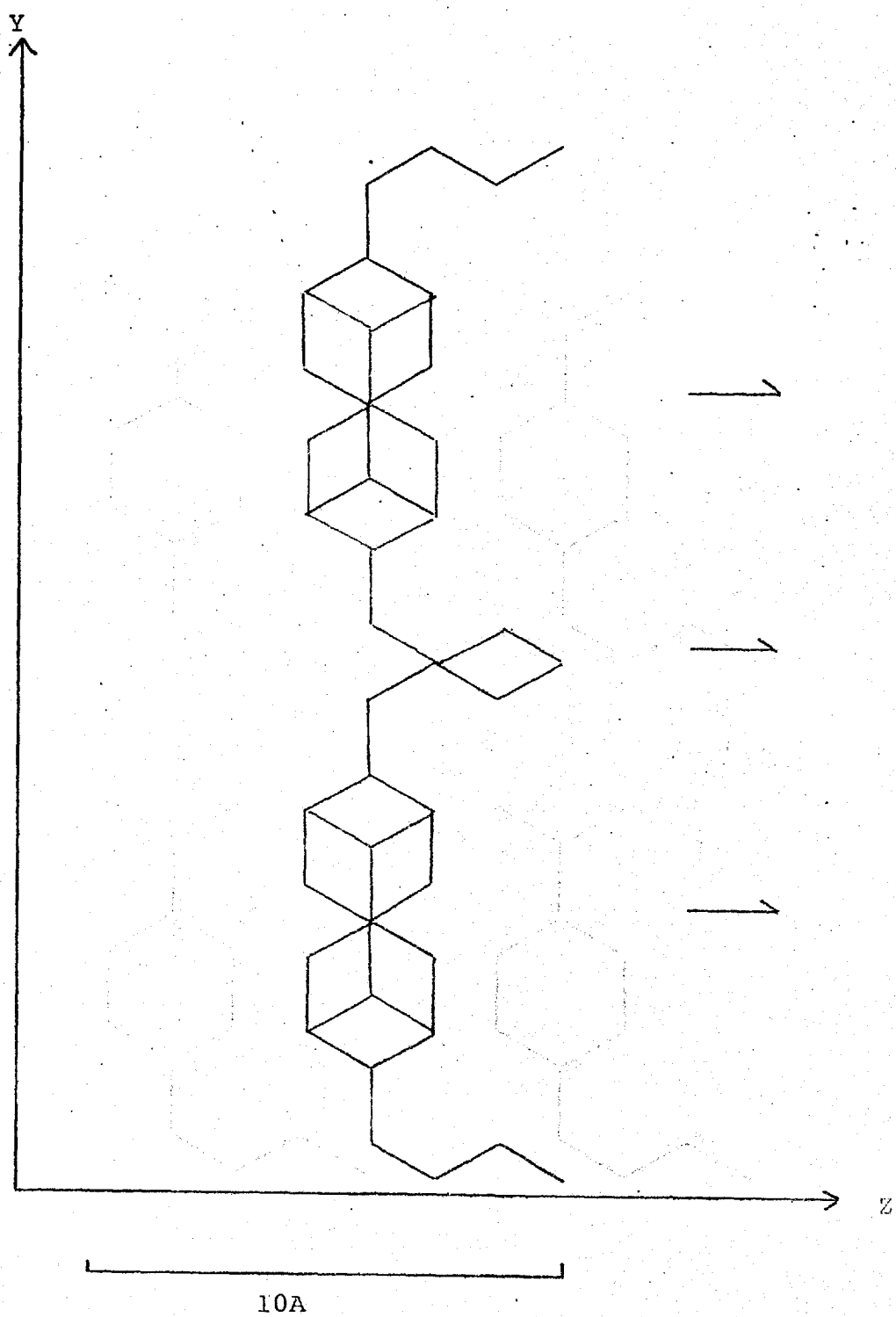
$$\cos \beta > 0.74$$

$$\cos \gamma < 0.18$$

The optical properties have revealed a large anisotropy of the charge transfer transition in favour of the b axis. Another anisotropy, which was not considered above, is apparent in the relatively large pyroelectric and piezoelectric effects and also in the extremely polar crystal growth and habit. The pyroelectric effect shows a net polarization of the crystal in the ground state, which, by the molecular symmetry, can only be derived from c axis components of the molecular dipole moments. The inductive effect of the nitro group is mainly operative along the b axis; therefore any c axis dipole moment must be caused by the inductive effect of the carbonyl group. It is then proposed that the FNPH molecule in the solid is "L"-shaped, with the carbonyl group directed along the c axis. This conveniently explains the effects mentioned above and allows packing of the molecules into the unit cell as shown in Fig. 5.2. The structure shows possibilities of hydrogen bonding between the hydrazide hydrogen atoms and the carbonyl oxygen atoms of neighbouring molecules and predicts the observed cleavage planes perpendicular to a and b.

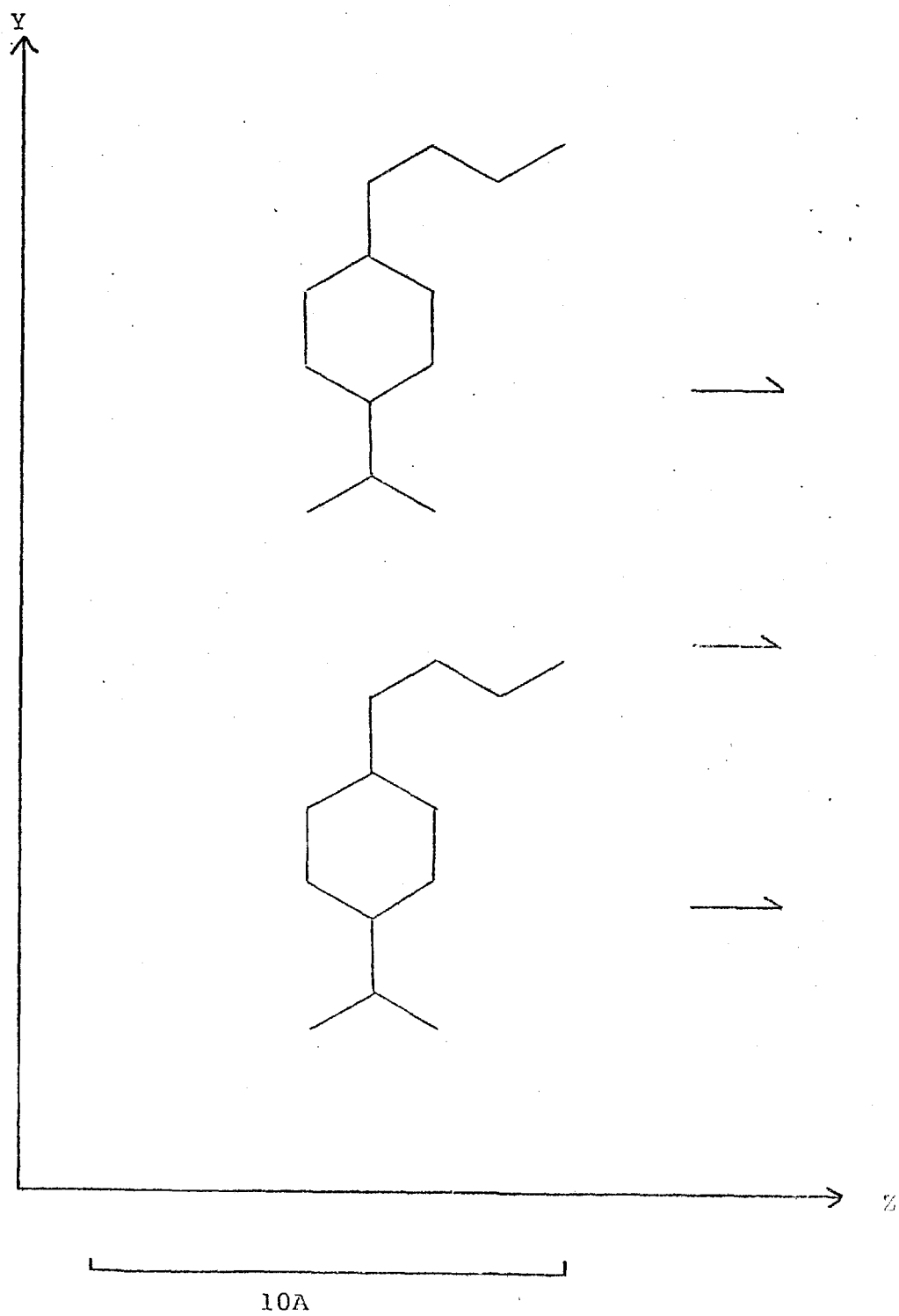
5.3. Non-linear Optical Effects of FNPH and Other Materials

The experimental work of Chapter 2 established FNPH and other compounds with charge transfer possibilities as efficient second harmonic generators in powder form. A number of similar works have since been published (Bolognesi (1973), Davydov (1973), Jerphagnon (1971), Bergman (1972)) and show similar results to this work. A general conclusion is that the S.H.G. is efficient only in the case of molecules containing acceptor groups, which promote charge transfer. The authors stress the importance of the absence of a centre of symmetry, but little mention is made of the extent of asymmetry, which cannot be estimated from a simple space group determination. This aspect will now be discussed in the case of FNPH with special reference to the electro-optic effect.



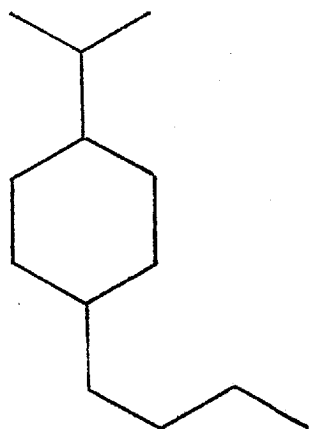
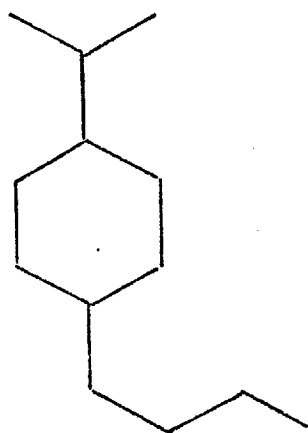
(C,N, and O atoms as in Fig.5.1)

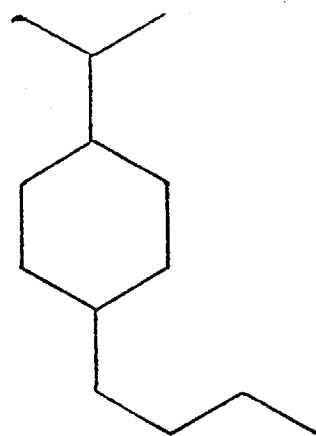
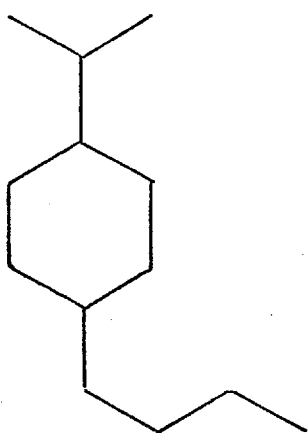
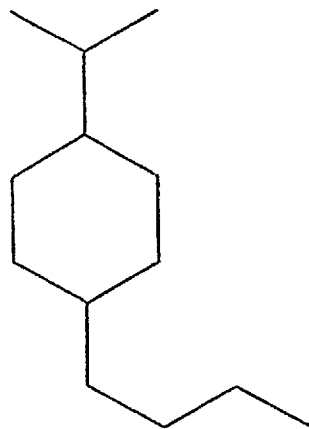
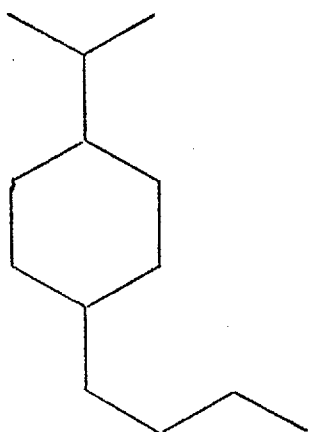
Fig.5.2 - A probable crystal structure of FNPH.

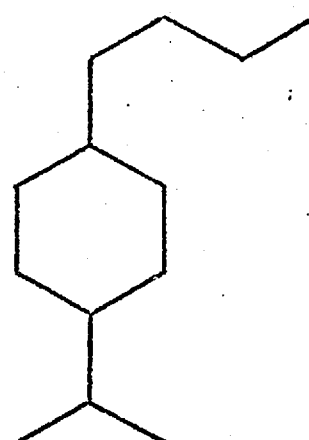
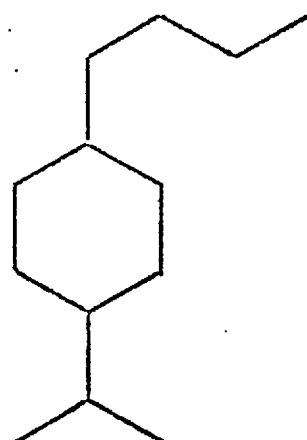
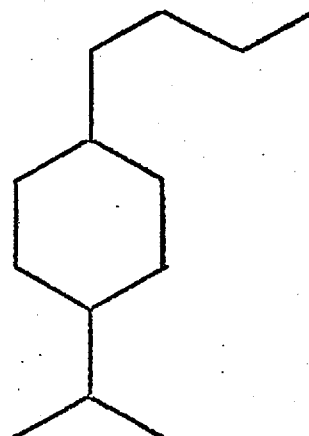
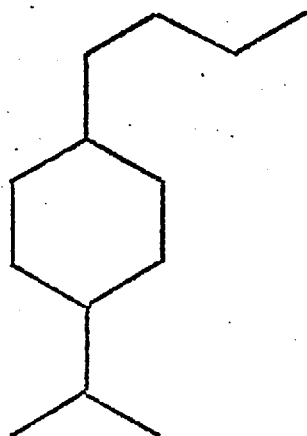


(C,N, and O atoms as in Fig.5.1)

Fig.5.2 - A probable crystal structure of FNPH.







5.4. The Electro-optic Effect of FNPB

In the electrochromic effect of MNA and the published SHG results mentioned above, there is considerable evidence that non-linear optical effects originate in an interaction of the applied field with the charge transfer transition. In Chapter 1 a possible mechanism of interaction was seen as a change in the transition energy due to the applied field:

$$\Delta \epsilon = \beta' E(0) \Delta \mu$$

$$\Delta \mu = \text{transition moment}$$

$$\beta' E(0) = \text{effective field.}$$

In crystals of point group mm2, only the Z axis component of the transition moment can be effective in this kind of interaction, since energy changes due to components along other axes would mutually cancel by symmetry. If we assume an electro-chromic shift due to a field along the Z axis, the following calculation derives an expression for the consequent electro-optic effect

$$\frac{d\omega_o}{dE_3} = k$$

$$\frac{d(\omega_o^2 - \omega^2)^{-1}}{dE_3} = -2\omega_o k (\omega_o^2 - \omega^2)^{-2}$$

From the simple Sellmeier theory:

$$n_i^2 - 1 = z_i \simeq B f_i (\omega_o^2 - \omega^2)$$

$$\frac{dn_i^2}{dE_3} = B f_i \frac{d(\omega_o^2 - \omega^2)^{-1}}{dE} = -2\omega_o k B f_i (\omega_o^2 - \omega^2)^{-2}$$

$$\begin{aligned}\frac{dn_i}{dE_3} &= \frac{1}{2n_i} \cdot \frac{dn_i^2}{dE_3} \\ &= -\omega_o k B (\omega_o^2 - \omega^2)^{-2} \cdot \frac{(f_i)}{(n_i)} \\ \text{and } \Delta_{ij} \frac{(dn_i)}{(dE_3)} &= -\omega_o k B (\omega_o^2 - \omega^2)^{-2} \cdot \Delta_{ij} \frac{(f_i)}{(n_i)}\end{aligned}$$

The final equation shows the relative electro-optic retardation between two principal axes, an important quantity from the device point of view since it is inversely proportional to the half-wave voltage. The expression contains k and therefore indicates the importance of a large component of the transition moment in the polar axis. The other parameter of interest is $\Delta_{ij} \frac{(f_i)}{(n_i)}$. This shows the effect of a natural birefringence and indicates the effect of the orientation of transition moment with respect to the three axes; for example, a transition moment with an equal component along each axis would give rise to only a small electro-optic effect since the difference of any two refractive indices would change very little.

A superficial view of the crystal structure as shown in Fig. 5.2 would suggest that FNPH, would show only a small electro-optic effect since direct perturbation of the transition energy by an externally applied field would be minimal. However, the experimentally determined values show that the effect in FNPH is almost as great as in MNA, where nearly half the transition moment acts along the c axis (Stevenson (1973)). One possible enhancement of the electro-optic effect in FNPH is via an applied inductive effect in the formylhydrazide group, i.e. the applied field can reinforce or oppose the inductive effect already present, thus perturbing the transition energy. By this mechanism the transition, which is mainly polarized

along the b axis, could suffer an electrochromic shift due to a field along the c axis.

Values of $\frac{f_i}{n_i}$ for FNPB are:

$$\frac{f_a}{n_a} = c. \frac{0.18}{1.64} ; \quad \frac{f_b}{n_b} = c. \frac{0.74}{1.9} ; \quad \frac{f_c}{n_c} = c. \frac{0.07}{1.60}$$

$$\frac{f_a}{n_a} = 1.10 \text{ c} ; \quad \frac{f_b}{n_b} = 3.89 \text{ c} ; \quad \frac{f_c}{n_c} = 0.44 \text{ c}.$$

$$\Delta_{13} \left(\frac{dn_i}{dE_3} \right) = 0.66 \text{ c} ; \quad \Delta_{23} \left(\frac{dn_i}{dE_3} \right) = 3.45 \text{ c}.$$

These values suggest that $V_{\lambda/2}^{13} \approx V_{\lambda/2}^{23} \times 5$.

The observed values in the D.C. mode were in the ratio $V_{\lambda/2}^{13} : V_{\lambda/2}^{23} = 2 : 1$, thus confirming the theory qualitatively, but at 1 MHz the voltages were equal. Clearly, the simple theory does not successfully predict the electro-optic behaviour.

The difference in half-wave voltages between the D.C. and high frequency modes suggests that there is a large secondary electro-optic effect. The pure primary electro-optic effect would be observed only in a condition of constant strain. A secondary effect arises from the combination of the converse piezoelectric effect and the piezo-optic effect (Nye (1957)). Provided that no piezo-electric resonances occur, the secondary effect would be reduced at high frequencies. A comparison of d.c. and h.f. results implies that the secondary and primary effects oppose each other.

(A temperature dependent birefringence, or "pyro-optic" effect was observed during the measurements of half-wave voltages. This is probably largely due to a secondary effect formed from the coupling of the thermal expansion with the piezo-optic effect. Another

secondary effect may be formed by a combination of the pyroelectric effect and the electro-optic effect.)

The secondary electro-optic effect gives one explanation of the differences between theory and experiment. Other factors can contribute to the discrepancy:

- (1) The Sellmeier expression for the refractive index omits a correction for the difference between the applied field and the effective field. The Lorenz-Lorentz refractivity formula would perhaps be more accurate, but strictly applies to cubic structures. For the extremely anisotropic FNPB structure, further corrections would have to be made in a rigorous treatment.
- (2) The theory takes no account of any orientational polarizability of the solid molecules. At frequencies from d.c. up to, say, the far infrared 1×10^{12} Hz, a dipolar molecule may partially rotate from its equilibrium position in sympathy with the applied field. The oscillator strength should not, therefore, be regarded as a constant, but as a vector (or strictly a second-rank tensor) perturbed by an applied field through a polarizability tensor. (This mechanism is similar to the secondary electro-optic effect but differs in that it may operate at constant macroscopic strain.) Even above the natural vibration frequencies of the dipolar molecules, the transition moment itself can be perturbed in orientation as well as in energy. In terms of the electro-chromic effect, a shift of the maximum intensity of the absorption band could accompany the wavelength shift postulated by the simple theory.
- (3) Considering the possibility of hydrogen bonding, there is some scope for intramolecular charge transfer, evidence for which would not have been seen in the solution spectrum. If this were the case, the solid would show additional bands each having a

contribution to the optical and electro-optic effects.

5.5. Device Applicability of FNPH

FNPH is a contender both in the field of electro-optic modulator materials and in the second harmonic generator series of materials.

As explained in Chapter 1, the field of electro-optic modulator materials at present utilizes the KDP isomorphs and ferroelectric perovskites. The half-wave voltages of FNPH were not found to be below these materials, at least at frequencies up to 1 MHz, and therefore FNPH will not replace the current materials unless other aspects of FNPH prove favourable. One advantage FNPH may have is its resistance to laser damage, which severely limits the life of current electro-optic modulators. FNPH has a low vapour pressure and therefore suffers little surface degradation in contrast with MNA, which deteriorates rapidly in air. No laser damage was noticed in FNPH - neither in the continuous He-Ne beam nor in the high energy pulsed Nd:YAG laser, where KD*P was severely damaged. The cleavage planes are conveniently placed in FNPH, so that one may form the optical entry and exit faces by cleavage; then the other cleavage plane may be used to divide a single bar into a matched pair. The matched pair is particularly useful because it can be arranged so that the natural birefringence and the associated temperature drift will cancel.

FNPH perhaps holds most promise in the field of second harmonic generation. The powder results indicate that the efficiency is comparable with MNA and the other materials currently of interest. Laser damage effects, of paramount importance in S.H.G. where intense beams are involved, were not observed. With the regular appearance in the current literature of new S.H.G. materials discovered by the powder method, the limiting step before devices can be made will be

the crystal growth, for which surprisingly little work has been published. In the case of FNPB, relatively large crystals have been grown, which proves that the crystal growth is not, in this case, insuperable.

CHAPTER 6 - CONCLUSION

This work was initiated with the belief that the crystal growth of chosen compounds was little more than a formality, the major task being the discovery of materials with the required non-linear optical properties. Quite the opposite was found to be true - a substantial number of compounds gave very encouraging results in second harmonic generation tests, but because of an inherent chemical instability of the compounds and the extreme anisotropy of crystal habit in some cases, the crystal growth problem became formidable.

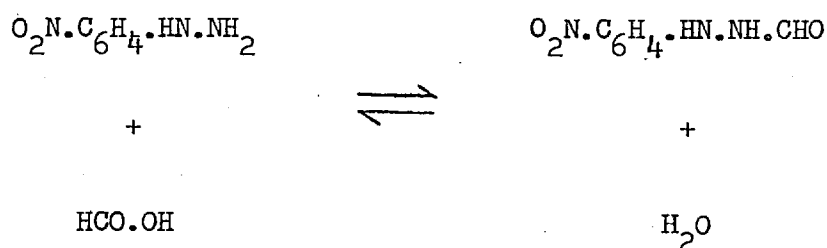
The most important materials characterized in this work were 4-nitrophenylhydrazine (NPH) and N-formyl-nitrophenylhydrazine (FNPH). The former showed a better second harmonic conversion efficiency than 3-nitroaniline (MNA) and the latter equalled MNA in efficiency. Although NPH was the more interesting material, only FNPH, which was chemically more stable, proved amenable to crystal growth.

FNPH was found to have reasonably competitive electro-optic properties, the best half-wave voltage being 12 KV. Although better half wave voltages are shown by many other materials, FNPH may have significant advantages with respect to device fabrication and lifetime. The same advantages may extend to the use of FNPH as a frequency doubler and further work in this context is well justified by the results of the SHG experiments on powder specimens.

An attempt was made to relate the non-linear effects of FNPH to some theoretical considerations, but meaningful correlations were elusive. Inevitably, the data and mathematical resources required for a theoretical treatment increase almost exponentially (non-linearly!) with the complexity of the molecules. Where the former is geared to the steady progress of research, the latter can blossom fruitfully in this particularly fertile ground!

APPENDIX IPreparation of FNPH

100g 4-nitrophenylhydrazine was placed in a 1ℓ conical flask. 100 ml formic acid was heated to its boiling point in a 250 ml flask then quickly added to the solid. On shaking the mixture, the solid dissolved to give a deep red solution. Within a few seconds a crystalline precipitate began to form. 200 ml absolute ethanol was added immediately and the mixture was shaken vigorously to disperse the crystallizing product. The bulky, orange precipitate was then filtered off and washed with 100 ml cold ethanol (yield = 100g = 83%).

Recrystallization

The whole of the solid was dissolved in 3ℓ boiling methanol, 10g activated charcoal added and the solution boiled for 30 mins. then filtered hot. When cool, the yellow crystals were filtered off, washed with diethyl ether then air-dried (yield = 70g). More solid was recovered by reducing the filtrate to 500 ml and crystallizing again to give a total yield of 90g.

The product was recrystallized again four times before using it for crystal growth experiments.

APPENDIX IIRelations between general and principal refractive indices

The refractive index ellipsoid may be expressed in cartesian co-ordinates:

$$\frac{x^2}{n_a^2} + \frac{y^2}{n_b^2} + \frac{z^2}{n_c^2} = 1 \quad (\text{A2.1})$$

In a general direction, the magnitude of the refractive index is,

$$n_\beta = (x^2 + y^2 + z^2)^{1/2} \quad (\text{A2.2})$$

Equation A2.1 may be written in parametric co-ordinates,

$$\begin{aligned} x &= n_a \cos \theta \\ y &= n_b \cos \phi \\ z &= n_c \cos \psi \end{aligned}$$

where θ, ϕ, ψ are the angles between the direction of the refractive index and the cartesian axes, X, Y and Z respectively.

Substituting in eqn. A2.2 we have:

$$n_\beta = (n_a^2 \cos^2 \theta + n_b^2 \cos^2 \phi + n_c^2 \cos^2 \psi)^{1/2}$$

$$\begin{aligned} \text{If } \cos \psi &= 0, \quad n_b^2 = \frac{n_\beta^2 - n_a^2 \cos^2 \theta}{\sin^2 \theta} \\ \text{If } \cos \theta &= 0, \quad n_b^2 = \frac{n_\beta^2 - n_c^2 \cos^2 \psi}{\sin^2 \psi} \end{aligned} \quad (\text{A2.3})$$

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