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Growth Perfection and Properties of Organic Non-Linear Materials*

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Abstract

Microminiaturization of optical circuitry requires electro-optic materials of far greater efficiency than even the best currently available. The skill of the synthetic chemist can be used to create molecules of virtually any structure. Given sufficient knowledge to allow a detailed specification to be described, these synthetic capabilities allow organic crystalline materials to be 'engineered' for optimum performance in a given context. The basic information allowing such crystal properties to be specified is currently extremely sparse. Nevertheless, already some fundamental principles of such 'engineering' can be described. New materials, with performances approaching those required, are listed and their growth as large single crystals is outlined. The availability of such large low-defect-concentration crystals is a prerequisite for accurate characterization, so that, for the first time, this is now possible. The way is open for the creation of a source of reliable data from which the theory governing the performance of these materials can be fully developed.

Introduction

Optical communication systems are increasingly displacing electronic methods because of their speed, bandwidth and reliability. However, at present they suffer from the difficulty that all-optical switching and routing are not possible on a microcircuit-sized scale. This problem arises from the rather low values of the electro-optic coefficients of currently favoured materials. For example (Broussoux *et al.*, 1989), in the case of the direct current (DC) (Pockels) effect, the efficiency of a material used in an optical modulator can be expressed as the number of degrees of phase shift per applied volt. For LiNbO₃ this is 0.05° V⁻¹ for a unit cube (the reduced half-wave-voltage dimension). In order to appreciate the scale of a device based on LiNbO₃, the voltage required for a phase shift of π , *i.e.* complete extinction, is

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Table 1. Comparison of electro-optic coefficients and half-wave voltages of organic and inorganic materials

Material*	r (pm V ⁻¹)	V_{π} (V)
Organic		
Urea	$r_{41} = 1.9$	
POM	$r_{52} = 5.1$	
<i>m</i> NA	$r_{33} = 16.7$	
MNA	$r_{12} = 67$	1300
DCNP	$r_{33} = 160$	370
PNP	$r_{12} = 13.1$	
Inorganic		
LiNbO ₃	$r_{33} = 30.1$	3500
KDP	$r_{63} = 26.4$	9300

See Sherwood (1990).

*POM: 3-methyl-4-nitropyridine.

*m*NA: *meta*-nitroaniline.

MNA: 2-methyl-4-nitroaniline.

DCNP: 2-(1-phenyl-4,5-dihydro-1*H*-pyrazol-3-yl)ethylene-1,1-dicarbonitrile.

PNP: 1-(5-nitro-2-pyridinyl)-2-pyrrolidinol.

KDP: potassium dihydrogen phosphate.

compatible with on-board transistor-transistor logic (TTL) circuit voltage if the ratio of layer thickness to length is $\sim 10^{-3}$. This means that, if the layer is 10 μm thick it would need to be 1 cm long! This precludes the possibility of packaging a large number of Mach-Zehnder modulators on a microchip-sized package (32 \times 15 mm). To achieve the necessary compactness of device, the electro-optic coefficient must be increased by a factor of at least 100. For several years now, attention has been focused on organic materials as a solution to this problem. The figure of merit associated with the DC non-linear effect is the reduced half-wave voltage V_{π} , *i.e.* the voltage required for a cube of the material to produce a phase shift of π . Already, organic materials such as DCNP [2-(1-phenyl-4,5-dihydro-1*H*-pyrazol-3-yl)ethylene-1,1-dicarbonitrile] (Table 1) have been produced with two orders-of-magnitude better performance than LiNbO₃.

The corresponding figure of merit for frequency doubling is the ratio d^2/n^3 . This arises from the efficiency of frequency doubled light generation in a χ^2 experiment. Again, in this quite different application, organic materials such as NPP [*N*-(4-nitro-

phenyl)-L-proline] have also been designed to have a two order-of-magnitude advantage over LiNbO_3 (Fig. 1). Indeed, such a figure of merit is 40 times higher than that of the best inorganic materials, potassium titanium phosphate and β -barium borate (Sherwood, 1990).

The high-frequency [second-harmonic generation (SHG)] effect depends on factors similar to those governing the DC effect, but is desirable for frequency-doubling lasers (e.g. from red to blue) to give robust compact blue or UV sources from lower-frequency laser diodes to be used in optical data storage, CD players *etc.*

The design of molecular structures

When electromagnetic radiation passes through a material, the oscillating electrical field, E , induces an oscillating dipole in the material and this is superimposed on any permanent dipole that it may possess. The induced dipole per unit volume, also referred to as the polarization, P , is a function of E and the electrical susceptibility, χ . The polarization may be expanded as a power series in E :

$$P = \epsilon_0[\chi^1 E + \chi^2 E^2 + \chi^3 E^3 + \dots] \quad (1)$$

(The tensor properties of the susceptibilities will be dealt with later.) The coefficients in this series for terms of higher order than first are very small and only achieve significance at extremely high field flux (W cm^{-2}). These are, however, the conditions of non-linear optical effects. The odd-power terms contribute to the polarization of all materials, but the second-

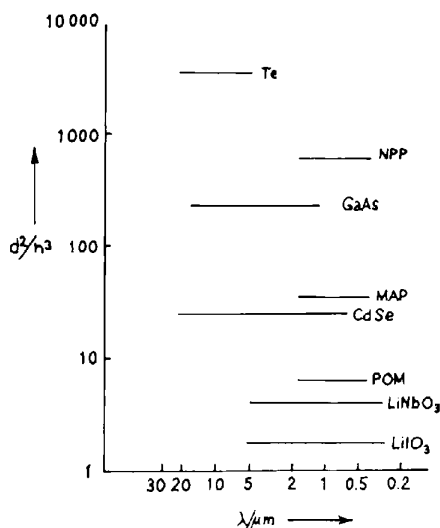


Fig. 1. The figure of merit d^2/n^3 (where d is the effective tensor element of χ^2 and n the refractive index) of organic compared with inorganic materials. NPP = *N*-(4-nitrophenyl)-L-proline; MAP = 2,4-dinitrophenyl-L-alanine methyl ester; POM = 3-methyl-4-nitropyridine.

order term, for example, is non-zero only for non-centrosymmetric space groups. Higher-order terms will not be relevant for the present discussion.

One major difference between inorganic and organic materials in the crystalline state is that organic materials preserve their molecular identity in the crystal, the molecules being held together by the comparatively weak dispersion forces. Accordingly, the molecular absorption spectrum will control the crystal's absorption spectrum and the polarizability of the crystal will be calculable from the molecular polarizability provided that the molecular arrangement in the unit cell is known. Calculations of crystal polarizability require the use of vector sums of the molecular properties modified by the internal field of the lattice caused by the neighbouring molecules. The Clausius-Mossotti (Lorentz-Lorentz) or Onsager approach is now superseded (in principle) by the sum-over-lattice-dipole methods in calculating non-linear response functions (Munn, 1988).

The search for superlative organic materials begins, therefore, with the search for molecules with large non-linear responses. The molecular parameters which parallel the crystal susceptibilities of (1) above are the linear susceptibility, α , and the non-linear hyperpolarizabilities, β , γ *etc.* If the tensor properties of the susceptibilities are neglected as before, the induced molecular dipole, $d\mu$, may be expanded as a power series in E :

$$\delta\mu = \alpha E + \beta E^2 + \gamma E^3 + \dots \quad (2)$$

As was the case for χ , β is non-zero only for non-centrosymmetric molecules. Additionally, β is primarily responsible for the large DC and high-frequency non-linear optical effects relevant to the communications industry. Non-centrosymmetry may be induced in a molecule by judicious substitution of a methyl group in a position off a molecular symmetry axis for example. However, this will not be very effective because the electronic distribution of the lowest-lying electronically excited state of the molecule has not been substantially perturbed. The quantity $\mu_e - \mu_g$, the change in permanent dipole on excitation from the ground (g) state to the lowest-lying excited state (e) is the best criterion of asymmetry induced by molecular substituents. This quantity is always zero for centrosymmetric molecules.

Second-harmonic generation in organic molecules is often described by a two-state model from which β can be deduced:

$$\beta = \frac{[3h^2/4\pi m][f_{ge}E_e(\mu_e - \mu_g)]}{[(E_e - h^2\nu^2)(E_e - 4h^2\nu^2)]}$$

Here, f_{ge} is the oscillator strength of the transition $g \rightarrow e$ and measures the degree of coupling of the external field, E , to this transition. The nature of the

denominators is such that the β value will tend to infinity when the transition frequency is approached by the external field frequency, ν , or its second harmonic 2ν . This dramatic increase in β is termed pre-resonant enhancement. In the case of SHG, it is thus desirable that 2ν approach the lowest-lying transition frequency. In practice, ν will not be close to the transition frequency, since the typical spectrum of any organic species exhibits increasing absorption as the UV is approached from the visible region. This would result in essentially total absorption of the 2ν frequency and an extremely lossy material.

From the above and simple particle-in-a-box quantum mechanics, it follows that molecules with extended conjugation path lengths will have low-lying transitions and should exhibit large β values providing that they are non-centrosymmetric. In 4-nitroaniline, the amino group is electron donating and the nitro group electron withdrawing, so that, in the ground state, there is considerable charge separation in the molecule with the amino end being positive. On excitation of the most intense transition in the visible spectrum, there is further transfer of electrons from the amino group into the conjugated system, $\mu_e - \mu_g = 22 \times 10^{-29}$ C m, the absorption band is at 320 nm and the consequent pre-resonant enhancement effectively doubles β for the frequency doubling of 1064 nm Nd/YAG (aluminium yttrium garnet) laser light to 532 nm.

Clearly, with the above concepts, it is possible to engineer a molecule to have the desired properties. For large molecules, the above polarizability calculations can only be performed by semi-empirical methods such as the sum-over-states technique (Docherty, Morley & Pugh, 1985; Pugh & Morley, 1987). The predictions of such calculations are in very good agreement with the electrical-field-induced second-harmonic generation (EFISH) measurements of β (Levine, 1977) (see Table 2 and Fig. 2).

Novel predictions have also been made by this method. For example, the discovery of the efficiency of the 2-pyrazoline ring structure as the intermediate conjugated system to which electron donating and withdrawing groups can be attached. Table 3 shows the effect of 1,3 substitution of this kernel.

This molecular effect is extremely weak, of course, and the practical use of such materials depends upon their alignment in a crystal. There is also the extremely important effect of the density of polarizability which is attainable in a crystal. In discussing the optimum crystal structure for these materials it is necessary to consider which effect is being targeted. To optimize the DC effect, the largest possible polarizability should be attained along one axis. It follows that the molecular dipoles should be parallel as far as possible. This is exemplified by 2-methyl-4-nitroaniline (MNA) (Lipscomb, Garito & Narang, 1981) and 2-(1-phenyl-4,5-dihydro-1H-pyrazol-3-yl)ethylene-1,1-dicarbo-

Table 2. Molecules for which calculated and experimental β values are compared in Fig. 2

Key	Name
1	Aniline
2	Nitrobenzene
3	4-Aminobenzonitrile
4	3-Nitroaniline
5	4-Nitroaniline
6	2,4-Dinitroaniline
7	4-Nitroanisole
*8	3-Methyl-4-nitropyridine <i>N</i> -oxide
9	(<i>E</i>)-4-Nitrostilbene
10	(<i>E</i>)-4'-Nitro-4-stilbenylamine
11	4-[2-(1-Methyl-4(1 <i>H</i>)-pyridinylidene)ethylidene]-2,5-cyclohexadien-1-one
12	<i>N,N</i> -Dimethyl-4-(2-nitrovinyl)phenylamine
13	<i>N,N</i> -Dimethyl-4-(4-nitro-1,3-butadienyl)aniline
14	Methyl <i>N</i> -(2,4-dinitrophenyl)alaninate
*15	1,3-Diphenyl-2-pyrazoline
*16	3-(4-Methoxyphenyl)-1-(4-nitrophenyl)-2-pyrazoline
*17	1-(4-Methoxyphenyl)-3-(4-nitrophenyl)-2-pyrazoline
18	(<i>E</i>)-4-Styrylpyridine
19	Fluorobenzene
*20	Indigo
*21	Pyridine
22	4-Dimethylaminocinnamaldehyde
23	4-[4-(4-Dimethylaminophenyl)-1,3-butadienyl]-benzonitrile

* These compounds were used to parameterize the computer program and have no β value.

nitrile (DCNP) (Allen, McLean, Gordon, Bothwell, Hursthouse & Karaulov, 1988). For these the reduced half-wave voltages needed for extinction are 1.3 kV and 370 V compared with the 2.9 kV of LiNbO₃.

For optimum second-harmonic-generation efficiency, however, phase matching of the fundamental and second-harmonic radiation is required. This necessitates the equality of the extraordinary refractive index of the fundamental and the ordinary refractive

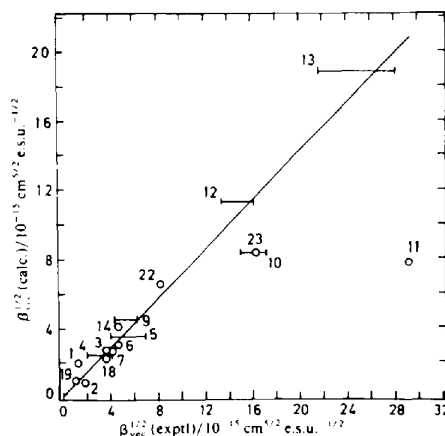
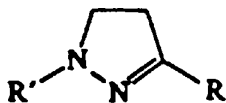


Fig. 2. A graph of calculated against observed hyperpolarizabilities. The square root of β is used merely as a graphical convenience to compress the span of the values. The error bars show the typical ranges of experimental values. The compounds are as listed in Table 2.

Table 3. The effect on β of 1,3 substitution on the 2-pyrazoline ring structure

β_0 is the value calculated at $\omega = 0$ to avoid resonance effects, β_ω is the value for input wavelength $\omega = 1.06 \mu\text{m}$



R	R'	β_0	β_ω
-H	-H	1.7	2.9
-NH ₂	-NO ₂	28.6	137.6
-Ph	-Ph	18.5	100.5
-Ph.NO ₂	-Ph.OMe	14	37
-Ph.OMe	-Ph.NO ₂	60.3	624
-CH=C(CN) ₂	-Ph	44.7	777.9

Table 4. Influence of the relative orientation of the molecules in the acentric lattice on the efficiency of phase matching

Material†	Space group	σ^* (°)	σ_m^* (°)	Powder SHG efficiency (urea = 1)
NMDA	$P2_1$	89.9	54.37	1
DAN	$P2_1$	70.8	54.37	115
NPP	$P2_1$	58.6	54.37	150

* σ is the angle between the molecular dipole and the b axis of the structure, σ_m is the optimum angle.

† NMDA: *N,N*-dimethyl-4-nitroaniline.

DAN: *N*-(2-dimethylamino-5-nitrophenyl)acetamide.

NPP: *N*-(4-nitrophenyl)-*L*-proline.

index of the second harmonic (type I) or that the average of the ordinary and extraordinary refractive indices of the fundamental equals the ordinary or extraordinary refractive index of the second harmonic (type II). Obviously, these conditions refer to two approximately orthogonal directions in the crystal (type I) or two at $\sim 45^\circ$ (type II) to each other. The optimum orientations of molecules in the lattice have been calculated for a range of structures (Zyss & Oudar, 1982). For the $P2_1$ structure the symmetry axis should lie at 54.37° to the molecular axes. The variation of efficiency in the compounds of Table 4 is largely due to this orientation effect.

Fig. 3 shows the crystal-packing diagrams of four organic materials. (1) is *N*-(2-dimethylamino-5-nitrophenyl)acetamide (DAN) (Baumert, Twieg, Bjorklund, Logan & Dirk, 1987; Kerkoc, Zgonik, Sutter, Brossard & Gunter, 1989; Twieg & Jain, 1983) and exhibits $\sim 115\times$ the SHG efficiency of urea. (2) shows *N,N*-dimethyl-4-nitroaniline (NMDA) and its much less-favourable packing angle (89.89°) compared with that for maximum effect, θ_m (54.74°) which leads to a SHG efficiency of only $1\times$ urea. (3) shows two projections of 2-(1-phenyl-4,5-dihydro-1*H*-pyrazol-3-yl)ethylene-1,1-dicarbonitrile (DCNP). This is ideally aligned for efficient Pockels effect and

has a half-wave voltage of $\sim 10\%$ that of LiNbO_3 . (4) shows *N*-(4-nitrophenyl)-*L*-proline (NPP) engineered for ideal SHG performance. Its efficiency is $150\times$ that of urea.

Both DCNP and NPP conform to optimal structural design as defined above. In NPP, intermolecular hydrogen bonds guarantee the head-to-tail configuration at near-optimum intermolecular angle. Both are examples of the successful engineering possible with organic materials.

The growth and perfection of organic crystals

The evaluation and use of non-linear optical crystals requires the availability of large single-crystalline specimens of high structural and optical perfection. A wide range of techniques has been developed for the growth of organic crystals from the melt, vapour phase and solution states (McArdle & Sherwood 1987). The criteria necessary for the control of defect structure have been defined (Sherwood, 1991) and the techniques have been applied to a wide range of organic solid types. Surprisingly little attention has been paid, however, to the growth of highly polar crystals such as are formed by the present materials (Badan, Hierle, Perigaud & Vidakovic, 1987).

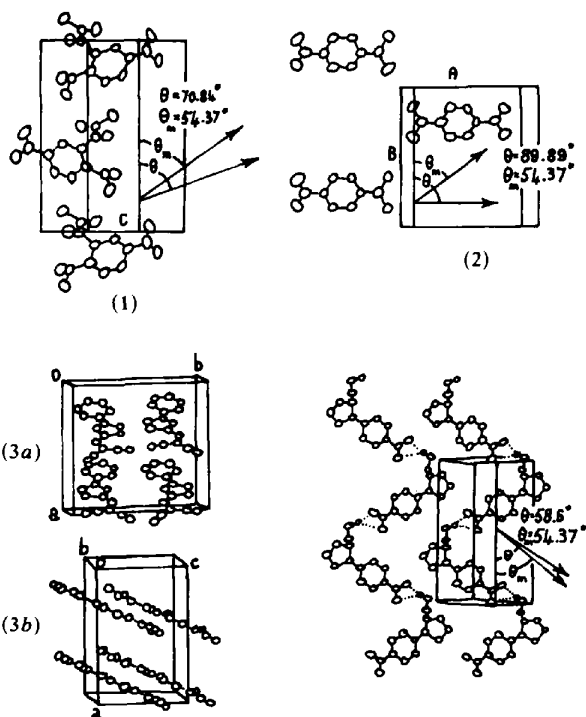


Fig. 3. Crystal packing diagrams of (1) DAN, (2) NMBA, (3) DCNP and (4) NPP. NMBA = *N*-(4-methylbenzylidene)-4-nitroaniline; other acronyms are detailed in the text. θ and θ_m are the angles between the crystal b axis and the molecular axis as observed and for maximum SHG efficiency, respectively.

Purification

A necessary pre-requisite for success in crystal growth is the availability of materials of the highest purity attainable. The large-scale synthetic procedures used to prepare organic compounds rarely yield material of purity greater than 98+%. Careful repetitive use of standard purification procedures (recrystallization, gradient sublimation, chromatography *etc.*) can raise this to 99.9%. If this is followed by the various forms of zone refining (melt, vapour or travelling solvent) then purities in excess of 99.999% can be achieved (McArdle & Sherwood, 1985).

The range of techniques which can be applied to the present materials is limited by their properties (instability on melting or sublimation, solvate formation on crystallization from solution *etc.*). Despite this, however, purities in the range 99.99–99.995% have been achieved (Badan *et al.*, 1987).

This level of purity has proved to be adequate for crystal growth.

Crystal growth

The principal requirement of the crystals is that they should be of large size, free from strain and imperfections and produced in a short time scale. This limits the method of production to low-temperature solution growth and melt growth. Vapour growth is a slow process and the method, which involves growth on a substrate, inevitably causes strain in the sample (McArdle & Sherwood, 1987).

Low-temperature solution growth near ambient temperature offers the best prospect of producing crystals under near-equilibrium conditions and free from strain and dislocations. Growth rates under ideal conditions are such that crystals of volume 10–100 cm³ can be prepared in periods of 1–4 weeks (McArdle & Sherwood, 1987). The alternative process, melt growth by the Bridgman technique, involves preparation in closed vessels under extreme temperature gradients around the melting temperature. Both constraints can result in the generation of strain and imperfection in the samples. Which method is chosen depends principally on the nature of the material. For example, urea and MBANP [*N*-(α -methylbenzyl)-5-nitro-2-pyridylamine] (Kondo, Ogasawara, Umegaki & Ito, 1988; Kondo, Morita, Ogasawara, Umegaki & Ito, 1989; Twieg, Jain, Cheng & Azema, 1982), two useful electro-optic materials, are highly unstable in the melt and decompose on sublimation. Thus, only solution-growth techniques can be used (McArdle & Sherwood, 1987).

Once the method has been defined, the next requirement is that a solvent should be found which allows prismatic growth and in which the solid shows both a moderate solubility (S_0) and solubility (S)/temperature (T) variation. The term moderate

has been defined as a solubility gradient ($dS/dT \div S_0 = 0.01\text{--}0.03 \text{ K}^{-1}$) (Hooper, McArdle, Narang & Sherwood, 1980). For both MBANP and urea the chosen solvent is methanol. Using seeded saturated solutions at initial temperatures of 303–313 K and slowly cooling these at rates of cooling within the range 0.05–0.5 K per day, one obtains the growth of excellent specimens in sizes up to 10×7×7 cm for MBANP (Fig. 4) and 5×4×4 cm for urea.

A major problem in attaining such sizes is that these highly polar solids show extreme growth-rate anisotropy. This inhibits the formation of large prismatic crystals and, if not controlled, yields needle-shaped or plate-like specimens. For example, MBANP under conditions of growth which should yield perfect specimens will not grow in the polar (y) direction. This places considerable constraints on the overall size of crystal which can be prepared. Any attempt to increase the growth rate, for example by increasing the supersaturation, causes unstable and imperfect growth to no advantage. The problem can only be solved by seed development. By developing seeds of the largest size possible then subsequent growth can be engineered to yield the large samples shown (Sherwood, 1989). Urea suffers a similar problem whereby unstable growth in the z direction inhibits the formation of faceting in the {111} planes. Here careful control of supersaturation is the solution to the problem. When this is achieved, capping of the {111} planes occurs and crystals of high perfection can be produced.

The crystal DAN presents more complex problems. This material decomposes in the melt and at high temperatures in the solid state. Its satisfactory solubility in methanol guides one to low-temperature solution growth. In this case, the anisotropy of growth is so marked however that large samples cannot be prepared from available seeds and the only methods which can be used satisfactorily are melt growth and vapour growth (Sherwood, 1989).

Luckily, as with many organic molecules, the rate of decomposition in the melt is low when the molten material is maintained close to the melting temperature and can be restricted provided that the material is not kept in the molten state for too long. Methods are available where this can be achieved (McArdle & Sherwood, 1987) and satisfactory crystals can be produced of higher quality than those prepared from solution. Equivalently, good crystals can be prepared from the vapour phase, but these are generally small and not suitable for cutting and polishing to yield the wide range of specimens required for optical evaluation.

Crystal perfection

It will be appreciated from the above that the crystal growth of these materials is not without its problems.

To make rapid progress with the growth programme and the improvement of the product requires an assessment technique which not only tells you that you have succeeded but helps you to achieve this. The ideal technique is X-ray topography practised using synchrotron radiation (Miltat, 1980). The laboratory-based technique with monochromatic radiation (Halfpenny & Sherwood, 1990) is equally useful but the spectral range and intensity of synchrotron radiation allows the rapid examination of crystals of relatively low quality. Consequently, the improvement in crystal quality can be followed from an early stage in the growth programme and the route to perfection can be planned more efficiently.

The two particular topographic techniques used are section topography and transmission topography (Miltat, 1980; Lang, 1978). The former allows the examination of the defect structure in a thin section of a bulk crystal without cutting. Excellent images can be obtained from diffraction signals after passage through several centimetres of organic crystal (Halfpenny & Sherwood, 1990). Successive exposures made by moving the beam along the crystal allows the defect structure at various points to be assessed without cutting the crystal into sections. In this way the growth history can be defined without introducing other damage into the crystal. This is most useful in defining the internal structure as, for example, in the urea crystal shown (Fig. 5). The nature and structure of the disordered volume in the z direction can be defined and strategies developed for overcoming this difficulty. This would not be possible if the crystal were cut into slices for transmission topography, since it would fall apart around the defective volume and this information would be lost. Such examinations also permit the isolation of regions of poor and good quality for eventual removal and optical examination.

Transmission topography is equally revealing but does involve the destruction of the crystal. The defect structure of particular portions of the crystal can be defined following removal and polishing for use. An example is shown of the quality of MBANP which has been achieved (Fig. 6). Urea can be grown to yield virtually perfect crystals with low-defect densities. The other materials always show an overall strain (defined by the dark contrast relative to that of the urea crystal) but well defined dislocations can be seen in the major growth sectors which allow the definition of (relatively) perfect and defect volumes for examination (Sherwood, 1989).

Such experiments define the structural quality of the materials. Optical characterization defines the optical quality.

Large crystals of this type are ideal for the detailed assessment of optical properties. They find limited use, however, for devices where more widespread use could be found for thin-film single crystals for wave guiding or single-crystal-cored fibres for direct use in telecommunications systems.

Although these are new areas of crystal-growth technology for organic materials, success has been achieved in the preparation of both alternative forms of the crystalline state. Large-area ($1\text{--}10\text{ cm}^2$) $5\text{--}10\text{ }\mu\text{m}$ thick single crystals of some materials have been prepared by adaptation of the Bridgman and solution growth techniques. Mono-mode crystal-cored fibres $5\text{--}10\text{ }\mu\text{m}$ diameter of high perfection and transmission and prepared by the Bridgman technique are also available (Rush, Holdcroft & Owens, 1988).

Characterization of crystals

It is highly desirable to have some method of screening crystal structures to determine whether they are non-centrosymmetric and, if so, whether they are likely to be significantly better non-linear optical materials than those currently known. Large single-crystal growth is a very slow process, so that a preliminary test for activity should not require oriented samples. The current technique is to perform a powder test for SHG. Initially investigated by Kurtz & Perry (1968), this test comes in several variations. It is possible to pack the sample as a polycrystalline powder into a cell on a microscope slide, cover this with a slip, and assess the SHG intensity when it is subjected to high-flux laser radiation. However, this method suffers from handling problems in that these strongly dipolar insulators charge readily and the electrostatic repulsion frequently causes the powder to fly out of the cell! Even if the cell is packed successfully, it will settle in time and the density of the powder in the laser beam will not be reproducible from day to day. A more convenient technique is to prepare the sample in the form of a 1% w/w loading in anhydrous Analar KCl pressed at $10.2 \times 10^3\text{ kg}$ in a 16 mm diameter die just as for infrared spectroscopy. The resultant disc can be tested for homogeneity by examining several sites across the disc and it is readily established that a homogeneous

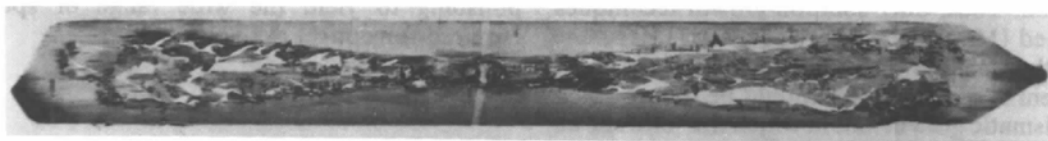


Fig. 5. A thin section topograph of a urea crystal showing defects concentrated in the core.

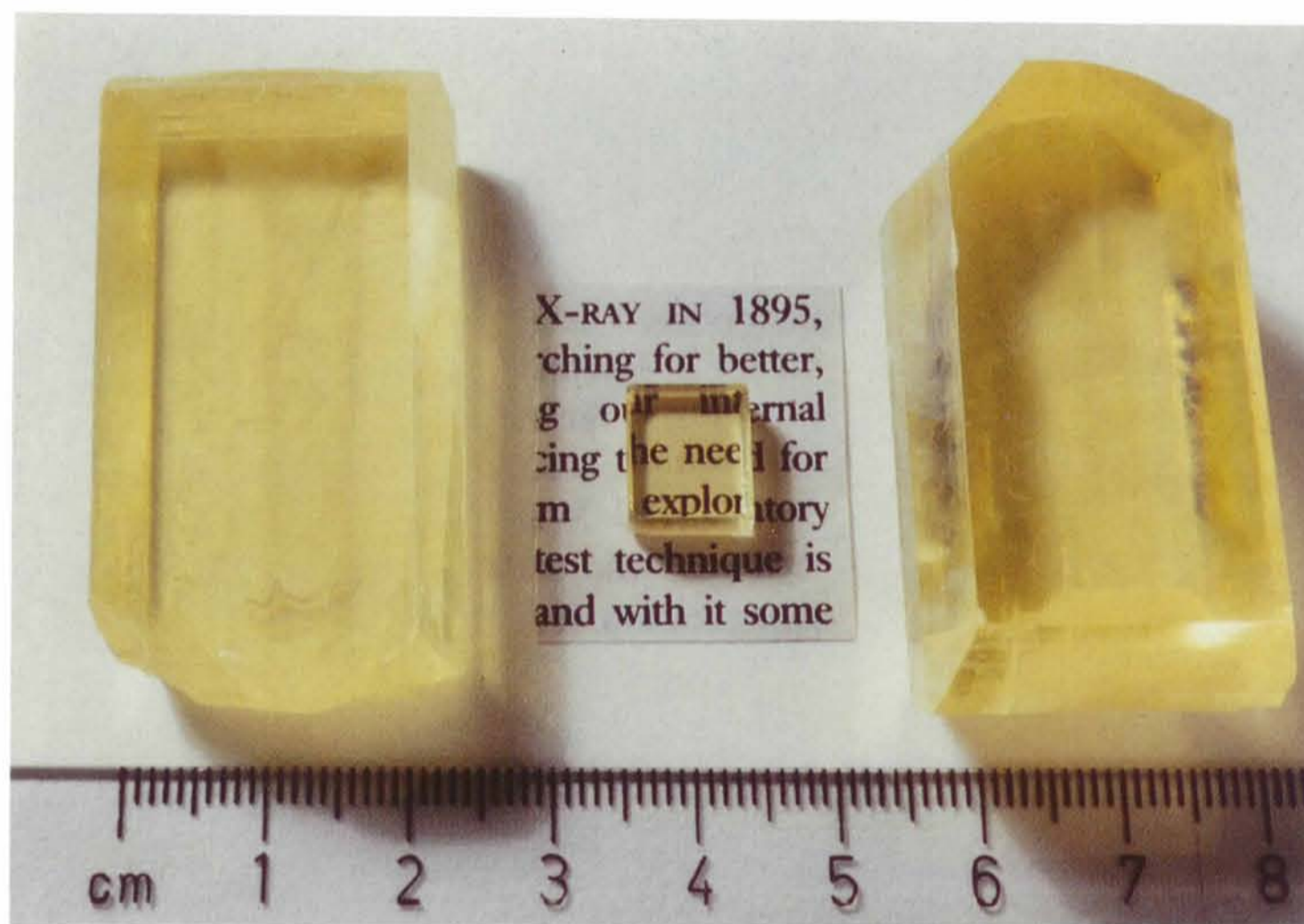


Fig. 4. MBANP crystals as grown and with a polished blank ready for Maker fringe analysis.

disc is easily produced (Bailey, Blaney, Cruickshank, Guthrie, Pugh & Sherwood, 1988). These discs give a reproducible result for many months provided they are stored in a desiccator. The general level of reproducibility ($\pm 25\%$) compares very favourably with other methods. Clearly, the crystal powder must not be so finely ground that the average particle size is much less than a coherence length [$\lambda/4(n_\omega - n_{2\omega})$ at normal incidence] for the SHG generation ($\sim 2 \mu\text{m}$ typically) otherwise there would be no signal. Fluctuations in particle-size distribution will thus cause irreproducibility in the signal. The powder could be graded for size, before preparing the disc, to reduce this problem. In our case, however, the laser beam at the focus was about five times the diameter ($1/e^2$) of the average crystal ($100 \mu\text{m}$), so that signals were averaged over several crystal sizes. A more serious problem is that the existence of phase matching in the material will generate signals several million times the non-phase-matched level. Should the phase-matched orientation be favourably aligned in the disc, the signal will be of far above average intensity and the significance of the material will be overestimated. This factor is extremely difficult to prevent totally and for this reason tables of relative performance established by any of the powder techniques are subject to very large errors. Such relative performance can only be established by a full single-crystal characterization requiring large extremely high-quality crystals as sources of well finished optical blanks.

Characterization of the performance of organic optically non-linear single crystals begins with a complete X-ray structure determination and the measurement of the linear principal refractive indices at both fundamental and harmonic wavelengths. This is done by a wide variety of methods including the Becke line microscopic technique (Hartshorne & Stuart, 1964) and Abbe refractometry. Both these methods require the use of fluids and, particularly for the high refractive indices of the organic materials, these fluids are frequently good solvents for the crystal! 'Dry' techniques include reflectance spectroscopy and minimum deviation measurements on a prism



Fig. 6. A transmission topograph of a MBANP crystal showing near-perfect lateral sectors and upper and lower sectors with a high number of defects.

cut from a large boule and optically finished. For the high accuracy ($\pm 0.001\%$) required to allow meaningful calculation of the phase-matching locus, the prism method is preferable although it is extremely time consuming. It has the further advantage that the refractive index is easily obtained over a range of wavelengths, permitting Sellmeier curves to be used to extrapolate to fundamental infrared wavelengths. Unfortunately, from any one prism only the axial refractive index is obtained with high accuracy. Although the orthogonal refractive indices can be determined, in principle, by solving simultaneous equations, the accuracy is only moderate ($\pm 1\%$) for the index most nearly parallel to the input face of the prism and very poor for the other index ($\pm \sim 50\%$). The prism faces must be flat to $\lambda/10$ with a small apex angle to avoid total internal reflection. This angle must be known to about 0.1° . The prism axis must be parallel to one of the principal dielectric axes to similar precision. Such orientation is best carried out by X-ray 180° back scattering Laue methods, combined with well referenced polishing jigs. Crystal blanks parallel ($\pm 30''$) to the (100), (010) and (001) faces are prepared in a similar way.

Single-crystal SHG characterizations consists of measurement of the Maker fringes observed when an optically flat and parallel blank is rotated about a principal dielectric axis oriented to be parallel to the incident laser polarization (Maker, Terhune, Nisenhoff & Savage, 1962). The elements of the χ^2 tensor are deduced from the incident polarization, the emergent second-harmonic polarization and the amplitude of the envelope of these fringes at 0° incidence angle. The pattern of non-zero elements in the χ^2 tensor is determined by the symmetry of the crystal in the same manner as the piezoelectric tensor (Nye, 1964). As yet, analysis of a triclinic crystal has not been necessary, so that only crystals with symmetries down to monoclinic have been analysed in detail (Pugh & Pavlides, 1990). Essentially, these fringes give the coherence length but, at low angles of incidence, the spacing can be used to obtain the sample thickness, L , with interferometric precision. This then allows the determination of the difference in refractive indices for fundamental and second-harmonic wavelengths with high precision. The latter is best obtained from a plot of fringe number against $\sin^2 \theta$ where θ is the angle of incidence. This yields a straight line of slope $L/\lambda[f(2\omega) - f(\omega)]$. For ordinary rays, $f(\omega) = 1/n(\omega)$ and, for extraordinary rays, $f(\omega) = [n(\omega)]$ in incidence plane and face of the sample]/ $[n(\omega)^2$ in the direction normal to the sample face].

A typical set of fringes is shown in Fig. 7.

One common problem with organic materials is the comparatively poor zero data obtained for Maker fringes. There is no difficulty, in the case of quartz, in obtaining ± 1 bit resolution of the zero positions.

The reason for this difficulty is not clear as yet, but it is undoubtedly significant that the coherence lengths of these materials are typically an order of magnitude less than that of quartz. Additionally, their hardnesses are around Mho 1, making it extremely difficult to polish these materials to the same quality of finish as quartz. The strain level and thus defect concentration in these materials is also far higher than in quartz. This leads to light scattering at a higher level, especially from polished blanks cut from large boules. Cleaved samples from small unworked crystals seem to result occasionally in better zeros, but limit analyses to principal cleavage planes (Kondo *et al.*, 1988). The Maker fringe apparatus is shown in Fig. 8.

In addition to d_{ij} determination, this equipment, with suitable neutral density filters on the photomultiplier tubes, can be used to find points on the phase-matching locus. There are two types of phase matching. In type I, the extraordinary refractive index of the fundamental equals the ordinary index of the second harmonic or *vice versa*. In type II the average of the ordinary and extraordinary refractive indices of the fundamental equals the ordinary or extraordinary index of the second harmonic. To detect type I phase matching, the incident fundamental and emergent second-harmonic polarizations are orthogonal. Type II is detected by aligning the incident fundamental polarization at 45° to the rotation axis and analysing one or other of the parallel or orthogonal second-harmonic polarizations. The angles of incidence at which these phase-matching signals are detected are extremely valuable tests of the accuracy of the linear-refractive-index values obtained earlier. Indeed, such information is often essential to refine the accuracy of the refractive-index data.

Structure-property relationships

The angular dependence of the phase-matched second-harmonic intensity is often used as a criterion of perfection for non-linear optical crystals. Fig. 9

shows such curves for two sectors of the (001) face of MBANP.

These two sectors are clearly shown in the topograph of Fig. 6. The crystal is divided roughly diagonally into four sectors. Top and bottom sectors have much higher defect concentrations than the left- and right-hand lateral sectors.

If the plots are reduced to the same scale, there is indeed a considerable difference in the quality of fit. Of course, the more perfect region gives three times more efficiency of second-harmonic generation. Clearly the defect density has a marked effect on the efficiency of SHG generation. The defect density of the organic non-linear optical materials is considerably higher than that of less-polar organic crystals for reasons discussed above and this certainly means that the present performance is not yet optimized for these materials.

At the moment, there are very few data on the thickness and power-flux dependence of the SHG efficiency of organic materials. In the case of *N*-(2-dimethylamino-5-nitrophenyl)acetamide (DAN), the efficiency rises to a maximum of 30–35% at 1.5 mm thickness for a sample oriented so that phase matching occurs at normal incidence. The sample in this test was anti-reflection coated by conventional vacuum evaporation techniques, showing that such materials are susceptible to some normal fabrication methods (Kolinsky, Bailey, Cruickshank, Pugh & Sherwood, 1991). The power flux level used here was $\sim 150 \text{ MW cm}^{-2}$. The efficiency rose to 30–35% at this power density and remained constant up to the highest level tested ($\sim 400 \text{ MW cm}^{-2}$).

The performance of organic materials in Pockels switching has been assessed in only a few cases. The spectacular half-wave voltage of MNA has already been mentioned.

DCNP was designed from theoretical predictions. The half-wave voltage, $V(\pi)$, varies with wavelength for this material as shown in Table 5. The effect of pre-resonant enhancement is clearly seen with the dramatic increase in r_{33} as the absorption edge is approached (Allen, 1989).

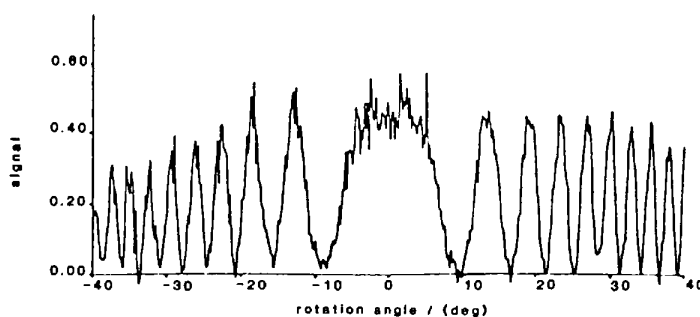


Fig. 7. Maker fringes obtained with both 532 and 1064 nm light polarized parallel to the z dielectric rotation axis. The signal is relative to the maximum intensity generated by d_{11} of quartz.

There is a belief that, because organic materials are soft and have comparatively low melting points, they must be more susceptible than inorganic materials to optical damage. There is no real evidence

to support this belief. If one remembers that the defect density in materials produced so far is not yet optimized, the current damage thresholds in excess of 500 MW cm^{-2} are extremely high. The assessment of optical damage thresholds in these very anisotropic crystals must take account of their pleochroic absorption spectra. Preliminary data for *N*-(α -methylbenzyl)-5-nitro-2-pyridylamine (MBANP) are shown in Table 6.

The thermal diffusivity was measured by the thermal reflection technique (Bailey, Cruickshank, Pugh & McLeod, 1982) and is expressed as rate constants in s^{-1} . The amplitude quoted is that of the probe laser modulation. This technique offers the ability to observe the onset of optical damage before it reaches destructive proportions as well as giving thermal diffusivities along the principal dielectric axes of the crystal. Thermal-expansion sensors are also becoming available for this material allowing the temperature rise to be calculated. As expected, the stresses in these materials are also highly anisotropic. It is found that the lowest damage thresholds in this material are not in the directions where the largest surface distortions (and therefore energy absorptions) occur. The details of the damage mechanism are still under investigation, but it is clear that a simple statement of one damage threshold will not be possible for these materials.

In crystal-cored fibres, in which the organic non-linear material is grown in the hollow silica fibre by the Bridgman technique, MNA shows particular promise in that its *b* axis lies along the fibre. This allows access to the high $d_{11} \chi^2$ element. However, the insertion loss is $13\text{--}25 \text{ dB cm}^{-1}$, arising from poor cleavage at the input and output faces because the easy cleavage plane is (103). Additionally, defects and voids occur within the crystal core, producing a very high scatter level. With better-quality crystals such as benzil and *meta*-nitroaniline (*mNA*), insertion losses are around 2 dB cm^{-1} . Compared with single crystals, this core gives $1.6 \times 10^{-4}\%$ SHG efficiency at 532 nm with 50 W peak input power in

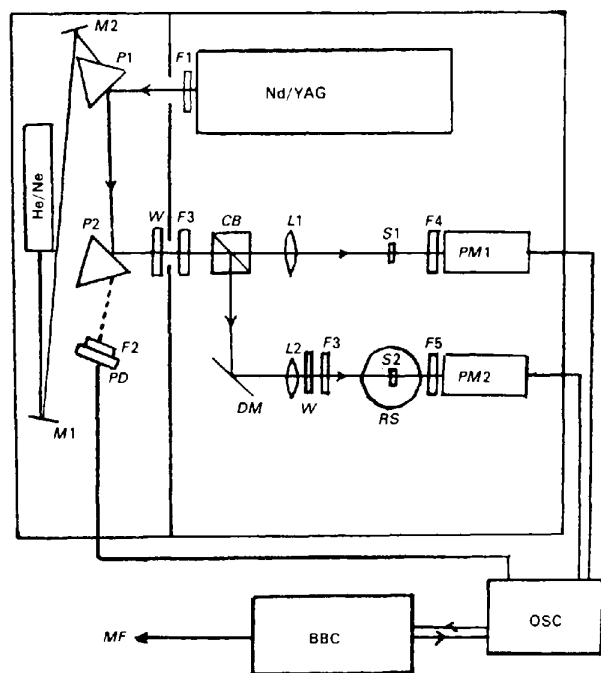


Fig. 8. The Maker fringe apparatus. *F1* is a filter to block the laser Xe arc radiation, *P1* and *P2* are attenuating prisms, *F2* is an attenuating filter and *PD* is a fast photodiode used to trigger the electronics. *W* elements are $\lambda/2$ plates used to balance the laser intensity in the two arms of the experiment and rotate polarization; filters *F3* block 532 nm radiation, *CB* is a beam splitting polarizing cube, *DM* a dielectric mirror for 1064 nm light, *L1*, *L2* are lenses of 50 nm focal length, *S1* a quartz reference crystal oriented to generate 532 nm light from d_{11} , *S2* the sample crystal, *RS* a computer-driven high-resolution stage, filters *F4* and *F5* are 532 nm narrow-band-pass filters, *PM1* and *PM2* are high-gain photomultipliers with 2 ns rise times, *OSC* is a fast digitizing waveform averaging oscilloscope controlled by microcomputer, *BBC*, via IEEE bus, *MF* is a link to the main-frame computer.

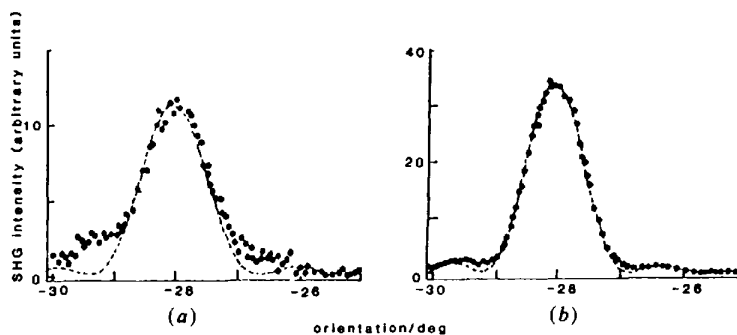


Fig. 9. (a) is the phase-matched peak shape observed for MBANP (001) compared with the theoretical shape, for imperfect upper and lower sectors of Fig. 6; (b) shows the same curves for the perfect lateral sectors. Note the increased efficiency for the latter sector.

Table 5. Wavelength dependence of half-wave voltage and electro-optic coefficient of DCNP

Wavelength (nm)	V(π) (V)	r_{33} (pm V ⁻¹)
629	340	78
633	375	71
640	411	69
730	1181	35
1084	3734	28
1152	3870	30

DCNP: 2-(1-phenyl-4,5-dihydro-1H-pyrazol-3-yl)ethylene-1,1-dicarbonitrile.

Table 6. Directional dependence of thermal diffusivity and amplitude of thermal reflection signal in MBANP

Laser polarization	Diffusivity vector	Thermal diffusivity	Amplitude (%)
Perpendicular to Y	Parallel to Y	7	7
Perpendicular to Y	Perpendicular to Y	9.5	11
Parallel to Y	Parallel to Y	7	56

MBANP: N-(α -methylbenzyl)-5-nitro-2-pyridylamine.

a 6–10 μm diameter core for a fibre length of 12 mm (Nayar, White, Holdcroft & Sherwood, 1987).

Concluding remarks

The potential of organics as non-linear optical materials is clear from the above discussion. Their great merit lies in the ability of chemists to 'engineer' their spectra and structures at will. Unfortunately, it is also clear that there is a great need for further information on several families of structures in order to understand more fully the factors leading to acentric structures, good growth habits, high damage thresholds and d_{ij} oriented in the best directions for DC or SHG device exploitation. These materials require some new technology in crystal growth and optical finishing, but can also be treated by conventional methods as in coating by vacuum evaporation. Optical fibre coupling methods need to be developed to cut down insertion losses, although it is already clear that reasonably high efficiencies in, for example, SHG can then be expected. The development of these materials is now at a watershed. If sufficient work is carried out on organics soon, their full potential will be realised in many all-optical micro-miniature devices. If such work is not done, a great opportunity will have been lost.

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The Evolution of Crystallography from the Paris 1954 to the Bordeaux 1990 Congress

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This year, as in 1954, the International Union of Crystallography has chosen France as host for its General Assembly. It is tempting to compare the two events. Modern crystallography started in 1912 with its discovery by M. von Laue: thus the 1954 Congress took place just half way between the very beginning of X-ray crystallography and now. So it is a good time to compare what has been realized in an equal period before and after 1954 and to appreciate the evolution of crystallography. On the other hand, the two Congresses have given to the crystallographic community similar 'excitations', a third of a century apart. A comparison of the responses may reveal changes of mind in society.

The President of the IUCr in 1954 was J. M. Bijvoet. The Presidents of the Congress were M. and L. de Broglie and Ch. Mauguin. The Secretary of State for Research who presided over the Opening Ceremony was H. Longchambon. He was a crystallographer; so today is Hubert Curien. Of course, in between there have been many Ministers of Research who were not crystallographers, or even scientists. But we are proud to see that men whose great talents have been recognized have chosen crystallography as their scientific discipline.

The organizing Committee was chaired by Jean Wyart; we regret that he could not be with us today, as we had expected. J. Wyart told me that the finances of the Congress had been so well managed that he had been able to give some money back to the Union. We know now the reason for this financial success: the treasurer was a young man named Hubert Curien.

In 1954, the number of participants was about 500; it is 1700 in 1990. Quite a few who are with us today also attended the previous meeting. These representatives of the older generation show that they maintain their interest in crystallographic advances. The great increase in the number of participants is, of course, not surprising. We observe, however, that the growth

factor is certainly less than the increase in the number of researchers in crystallographic laboratories or the increase in the number of annually published papers. This reflects a change of attitude of crystallographers towards Union Congresses. At the beginning of the Union (1948), crystallographers were working in a rather closed circle. Now they are working in laboratories for chemistry, physics, biology *etc.* in collaboration with colleagues of more and more varied backgrounds. Therefore, genuine crystallographers prefer to present their original works in specialized meetings: results discussed before specialists have a better chance to spread among interested people. For instance, in the early fifties, meetings in the domain of solid-state physics were rare whereas now plenty of them are organized each year.

So it is natural and, in fact, advantageous for a sound development of our discipline that the audience of the present and future Congresses of pure crystallography be self-restricted. However, periodical Congresses of the Union are essential: they are necessary because they bring together representatives of almost every crystallographic laboratory in the world. The success of the Bordeaux meeting proves that it fulfils a general need, to maintain the cohesion of crystallography and to facilitate the cross-fertilization of the various branches: somebody working in a laboratory for the physics of metals may find the solution to his problem in a paper by a colleague working with biologists. We can be reassured that there is no sign of a decline in the Union, even if the Congresses do not become enormous.

An important point is the partition of the participants from the different countries and also of the submitted abstracts. In 1954 the percentages were the following: UK 34, France 29, USA 12, Germany 11, Netherlands 7, Sweden 5 plus 21 countries below 5%. The striking feature is the predominance of the British delegation; the figure for France is distorted by the