

# Measurement and calculation of second-harmonic generation in single-crystal spheres: application to $d$ coefficients of D-mannitol, $C_6H_{14}O_6$

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**Abstract.** The measurement of  $d$  coefficients from second-harmonic efficiencies in crystal spheres is studied.  $KH_2PO_4$  is used as a reference for measurements in spheres and with the Maker-fringes technique. As an example, unknown  $d$  coefficients in an orthorhombic mannitol,  $C_6H_{14}O_6$ , in which large coefficients of optical rotation have recently been measured, are determined as  $d_{123} = 0.06(2) \text{ pm V}^{-1}$  and compared with a calculation performed with a dipole–dipole interaction model in which the effect of the electric field of a light wave on the crystal structure is applied. Modelling of the basic parameters in the calculation gives good agreement with the experimentally derived values. The accuracy in determining the  $d$  coefficients, achievable with spheres is limited to 20%.

## 1. Introduction

Maker *et al* (1962) described a technique which allows one to measure the coefficients of second-harmonic generation (SHG), the so-called  $d$  coefficients, with acceptable accuracy. This technique, which was refined by Jerphagnon and Kurtz (1970), still provides the best results, but one needs relatively large and well-polished sample plates.

More recently, Velsko (1989) published details of a technique for making direct measurements of the phase-matching properties of small single crystals, ground approximately into spheres and mounted at the centre of an Eulerian cradle. In this method the samples are immersed in index-matching fluids to reduce scattering from the uneven surface. It was claimed with this method that phase-matching angles could be determined to within  $\pm 1^\circ$ , angular acceptances to within 20% and effective  $d$  coefficients to within 25%. Similarly, Boulanger and Marnier (1989) published measurements of the walk-off angle as a function of the propagation direction and non-linear optical behaviour near the optical axes in  $KTiOPO_4$ , employing spheres of about 5 mm diameter in a two-circle goniometer. However, despite the promise of the authors at the end of the publication to extend the technique, so that non-linear coefficients can be measured from SHG efficiencies in different directions, to the best of our knowledge this has not been published so far. In very recent work (Boulanger *et al* 1994) the sphere technique was used to determine the relative signs of the  $d$  coefficients

of  $KTiOPO_4$ , the magnitudes of the coefficients still being measured by using crystal plates.

The aim of the present paper is to discuss measurements for spheres with  $KH_2PO_4$  as a reference and with mannitol,  $C_6H_{14}O_6$ , for which the  $d$  coefficients are not well known. Mannitol has large optical rotation coefficients (up to  $50^\circ \text{ mm}^{-1}$  at 600 nm). However, the coefficients of the electro-optical effect are rather small. Most of the optical properties of orthorhombic mannitol, which belongs to the Hobden class 9 (Hobden 1967), were recently described by Kaminsky and Glazer (1997), employing a new model, the dipole–dipole interaction electron-cloud shifting model, abbreviated as the DES model, based on the dipole–dipole model of Devarajan and Glazer (1986), to which the effect of an external electric field on the crystal structure was added. Using the measured values of the refractive indices of mannitol and the structural co-ordinates, the  $d$  coefficients were estimated to be small as well.

A preliminary experimental test on SHG was carried out (Fitzmaurice 1994), showing that the SHG signal was roughly of the expected magnitude (Fitzmaurice and Kaminsky 1995). However, a more accurate determination of the  $d$  coefficients is still necessary for further discussions of the model calculations.

A further unanswered question is that of to which substances the simple DES model of Kaminsky and Glazer (1996) is applicable. This model allows one to estimate the linear birefringence, optical gyration (circular birefringence) and  $d$  coefficients and, with the

help of experimental dielectric constants, to calculate electrogyration and electro-optical effects. In most cases, the magnitudes of the tensors that obey Neumann's principle are calculated with the correct sign. However, the model was developed to study relations between different effects for a given structure rather than to substitute for other commonly used theories such as the Miller-delta theory (Miller 1964, Robinson 1967), bond-charge theory (Levine 1973, Engel and Defregger 1991), ionic group theory (Chen 1979, Chen *et al* 1989, 1990) and hyperpolarizability models (Zyss 1993).

In this paper, we shall give a brief description of the theory of the SHG generation in crystal spheres. Secondly, the accuracy of measurements on spheres is compared with that of those from crystal plates, in both of which cases  $\text{KH}_2\text{PO}_4$  serves as a reference. Thirdly, the result for mannitol is discussed and compared with calculations with the DES model.

## 2. Theoretical considerations

### 2.1. The two-circle cradle

We assume that the wavevector  $\mathbf{k}$  is parallel to  $z$ , where  $\mathbf{x}$ ,  $\mathbf{y}$  and  $z$  are the axes of the Cartesian laboratory-reference system (see figure 1). The initial polarizations are  $E_1^L$  parallel to  $\mathbf{x}$  and  $E_2^L$  parallel to  $\mathbf{y}$ . A variation of the direction of the wavevector is introduced by rotation first about  $z$  by the angle  $\varphi$  and then about  $\mathbf{y}$  by the angle  $\nu$ . This results in

$$E_i^P = u_{ij} E_j^L \quad s_i = u_{ij} s_j^L$$

with  $s^L \parallel (0, 0, 1)^L$  the direction of the wavevector for  $\nu = \varphi = 0$ ,  $E^P$  the transformed initial polarization and  $\mathbf{u}$  the rotation matrix

$$\mathbf{u} = \begin{pmatrix} \cos \varphi \cos \nu & \sin \varphi & \cos \varphi \sin \nu \\ -\sin \varphi \cos \nu & \cos \varphi & -\sin \varphi \sin \nu \\ -\sin \nu & 0 & \cos \nu \end{pmatrix}.$$

If the whole crystal is mounted differently, we have to specify the matrix  $\mathbf{w}$  which transforms the direction  $\mathbf{s}$  according to  $s_i = w_{ij} u_{jk} s_k^L$ . Thus  $\mathbf{w}$  gives the transformation between the cradle and the physical reference system ( $\mathbf{e}_2 \parallel \mathbf{b}^*$ ,  $\mathbf{e}_3 \parallel \mathbf{c}$ ). (Direction cosines, which are related to the physical reference system  $\{\mathbf{e}_i\}$ , are written as  $(x, y, z)^P$ .) In this case  $E_i^P = w_{ij} u_{jk} E_k^L$ .

The angle  $\gamma$  between the calculated vibration mode  $E''(\omega)$  in the crystal (see the appendix) and the initial linear polarization  $E^P$  with  $E^L = (\sin \beta, \cos \beta, 0)^L$  is calculated from

$$\cos \gamma = \frac{E_i^P E_i''(\omega)}{E^P E''(\omega)}.$$

It follows that the SHG signal is modulated both for type I and for type II phase matching (Okada and Ieiri 1971) according to  $\cos^4 \gamma$  for type I and  $\cos^2 \gamma \sin^2 \gamma$  for type II. In the case of circularly polarized light we get only a quarter of the calculated efficiency. If the sample is prepared as a plane-parallel plate, we have to consider the effect of reflection on an inclined plate. The main

contribution is related to the reflection of the initial wave. The amplitudes of  $E_1^L$  and  $E_2^L$ , as well as the thickness of the sample, are changed by the rotation  $\nu$  according to the Fresnel equations and  $\cos^{-1}(\nu')$ , respectively.  $\nu'$  is the angle between the wavevector and the normal to the plate inside the sample. The neglect of further reflections will lead to errors of more than 10% if  $\nu'$  and the refractive indices are both high. Multiple reflections inside the sample plate can increase the signal. However, it is our experience with another optical effect (the Faraday effect) measured with crystal plates, which in theory exhibits a strong dependence on multiple reflections, that this is significant only in absolutely perfect plane-parallel and polished samples and is difficult to achieve with standard preparation techniques. However, in almost ideal samples, interference by multiple reflections similar to those of the Fabry-Pérot interferometer causes additional peaks in the observed SHG efficiency (Bechtold 1976).

### 2.2. Crystal spheres

If the sample is prepared as a polished sphere (Velsko 1989), the phase-matching acceptance angle is increased by confocal refraction. We may assume a Gaussian-shaped intensity profile for a laser beam of diameter  $D$ , leaving about 60% of the intensity within  $D/2$ . The focus  $f$  of the sphere is found from  $f = 0.5nd/(n-1)$ , where  $n$  is the average refractive index and  $d$  is the diameter of the sphere, which leads to  $f > d$  for realistic refractive indices. The maximum angular acceptance  $\alpha$  in a sphere is roughly estimated from

$$\alpha = \frac{D(n-1)}{2dn}$$

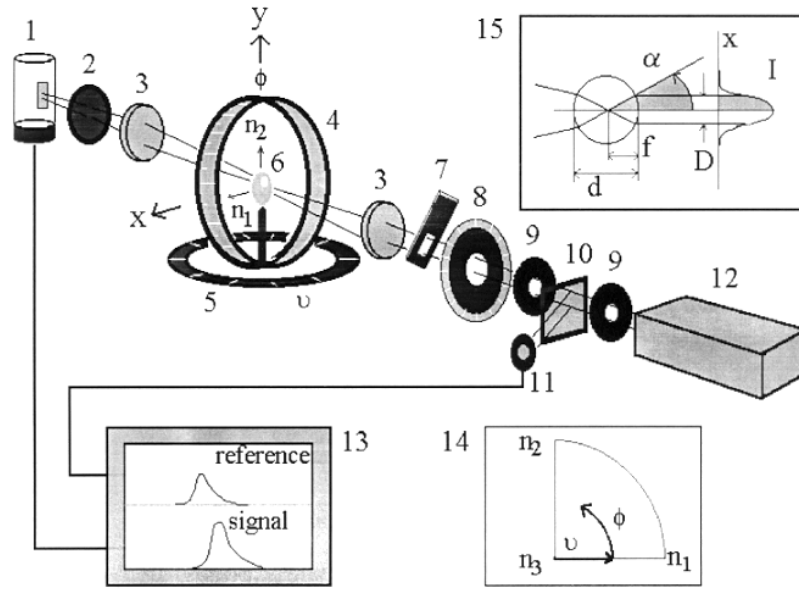
(with  $D = 2$  mm,  $d = 5$  mm and  $n = 1.5$ ,  $\alpha = 4^\circ$ ) which in general will be much larger than the angular acceptance of a plate of the same thickness. This results in an integrated phase-matching locus best represented by a Gaussian formula (see the appendix) if the acceptance angle of the sphere is much larger than that of the plate:

$$\frac{A}{L^2} e^{-x^2/w}$$

where  $w$  defines the width of the peak and  $x$  is the coherence length. The factor  $L^{-2}$  is introduced to conserve the independence of the SHG amplitude relative to the sample thickness  $L$ . Because  $x$  in general depends on the refractive indices, the value of  $w$  has to be fitted to match the calculated acceptance angle. The amplitude  $A$  is set so that the integrals below the two shaping functions are equal, which results in  $A = (\pi/w)^{1/2}$ . Although it has to be kept in mind that this is a very rough approximation, it has been shown that the area beneath the SHG matching peak is a precise measure of the SHG signal (Nash *et al* 1970).

The SHG efficiency changes with confocal refraction: the SHG signal is in proportion to  $I^2 \propto (D^{-2}(z))^2 \propto [4/D(1-z/f)]^4$ , where  $z$  is the distance along the wavevector from the initial side of the sphere. The SHG signal varies according to

$$\frac{I_{eff}^2}{I_0^2} \propto \frac{1}{d} \int_0^d \frac{dz}{(1-z/f)^4} \propto \frac{f}{d} \left(1 - \frac{d}{f}\right)^{-5}.$$



**Figure 1.** The experimental set-up: 1, photomultiplier; 2, 532 nm interference filter; 3, convex lenses; 4 and 5, cradle; 6, sample; 7, quarter-wave plate; 8, half-wave plate; 9, diaphragm; 10, beam-splitter; 11, reference photodiode; 12, Nd:YAG laser; 13, storage oscilloscope; 14, stereographic projection of the cradle angles and refractive indices in standard geometry; and 15, the acceptance angle (in mannitol and  $\text{KH}_2\text{PO}_4$ ;  $f$  is outside the sphere).

The ratio  $d/f = 2(n-1)/n$  depends only on the refractive indices.

### 2.3. The DES model

Second harmonics may be calculated from the shift of electron clouds surrounding the atoms induced by the field of the light wave. If  $\varepsilon_{ij}(0)$  are the relative dielectric constants without light and  $\varepsilon_{ij}(E^{light})$  those with the virtual light field, the difference

$$\varepsilon_{ij}(E_k^{light}) - \varepsilon_{ij}(0) = 2d_{ijk}E_k^{light}$$

gives the  $d$  coefficients. The relative dielectric constants for the wavelength  $\lambda$  of the initial infra-red light are calculated with the dipole-dipole model developed by Devarajan and Glazer (1986), which uses the crystal structure coordinates and the polarizability (strictly, in this paper  $\alpha$  is a polarizability volume)  $\alpha_{ij}$  of each atom inside the unit cell. The dispersion of  $\alpha_{ij}$  is roughly approximated by a  $\lambda^{-1/2}$  dependence. Because the model needs static fields and the field of the light wave varies sinusoidally, a static fraction ( $2/\pi$ ) of the field is taken to induce the virtual shift  $x$  of the electron cloud, which then is related to the polarizability of the  $k$ th atom by

$$x_i(k) = \frac{8\varepsilon_0}{e} \alpha_{ij}(k) E_j^{light}$$

where  $\alpha_{ij}$  is in  $\text{\AA}^3$ ,  $x$  in metres,  $E^{light}$  in  $\text{V m}^{-1}$ ,  $e$  is the charge of an electron in Coulombs and  $\varepsilon_0$  is the permittivity of free space. The commutativity of the last two indices in the  $d$  coefficients has to be applied artificially. Nevertheless the calculations automatically obey Neuman's rule. Because the dielectric constants are symmetrical,

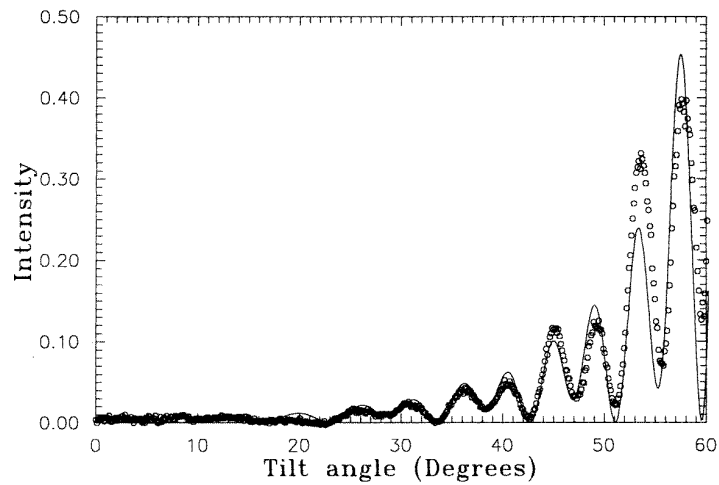
Kleinmann's rule (Kleinmann 1962) is followed, that is, the  $d$  tensor is totally symmetrical. This model had already been used successfully to calculate induced effects in some crystals, including mannitol (Kaminsky and Glazer 1997).

## 3. Experimental details

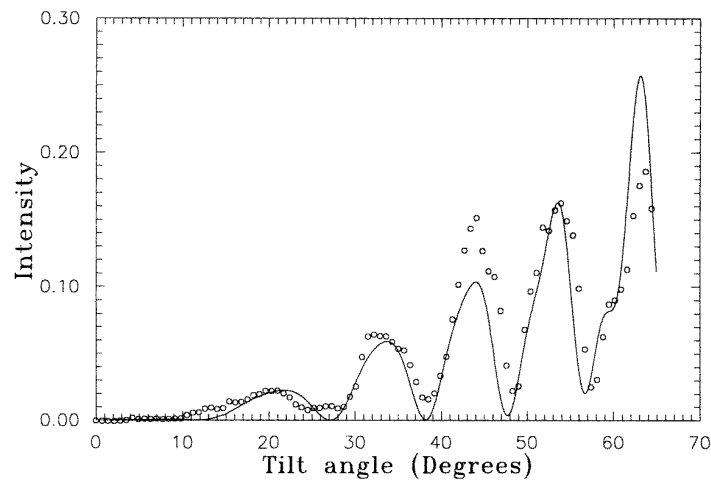
### 3.1. The set-up

The set-up to measure the SHG signals is shown in figure 1. The beam of a Nd:YAG laser (operating at  $1.064 \mu\text{m}$ ) is split to allow reference intensity measurements. The main part of the beam is passed through a half-wave plate and then focused onto the sample. The intensity behind the sample is collected with a confocal lens, passes through an infra-red filter, an optional neutral density filter and then a 532 nm interference filter and is fed into a photomultiplier. The reference diode and the photomultiplier are connected to a storage oscilloscope (Gould 4072) which is connected to a computer. The computer also drives the motors of the two-circle goniometer and determines the position of the half-wave plate with which the initial polarization is rotated. A quarter-wave plate can be inserted to produce circularly polarized light.

To make crystal spheres, a cube was first cut with a wet wire saw and then the corners of the cube were removed. The resulting shape was ground manually into a sphere using emery paper and then polished with  $\text{Cr}_2\text{O}_3$  on a polishing cloth. The minimum sphere diameter which could be treated in this way was about 5 mm. The quality of the spheres was such that the beam of a laser focused on the centre of the spheres was collected by a screen of 5 cm diameter at a distance 20 cm from the sphere for arbitrary orientation of the spheres. Plates were ground with  $5 \mu\text{m}$



**Figure 2.** Maker fringes of a  $\text{KH}_2\text{PO}_4$  sample plate cut on (001) with linear-polarized light. The thickness is 0.342(2) mm. The polarization angle  $\beta$  of the linear incident light was adjusted to give the maximum possible signal in the experiment and for the calculation. The wavevector was tilted from [001] towards [110].



**Figure 3.** Maker fringes of a  $\text{KH}_2\text{PO}_4$  sample plate cut on (001) with circularly polarized light. The thickness is 0.342(2) mm. The quarter-wave plate was inserted at  $45^\circ$  inclined towards  $y$ . The wavevector was tilted from [001] towards [110].

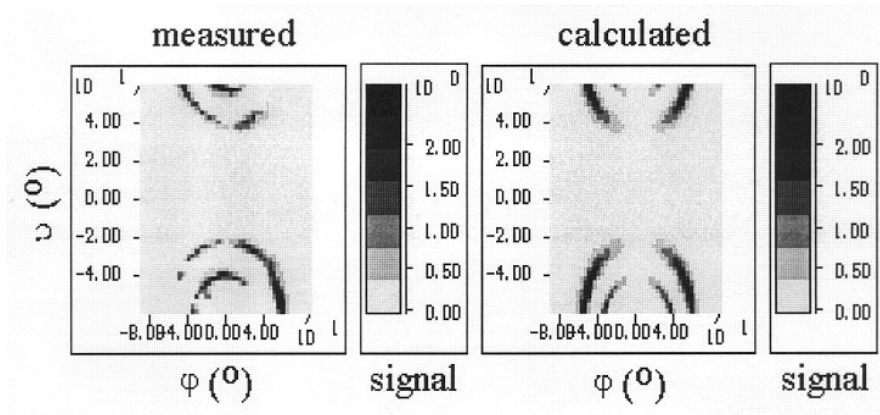
$\text{Al}_2\text{O}_3$  powder. The faces were polished on pitch with  $\text{Cr}_2\text{O}_3$  (polish green). Moisture introduced by breathing on the pitch lap at the same time helped to establish an optical finish resulting in clear surfaces being inclined less than  $2 \mu\text{m cm}^{-1}$  relative to each other.

### 3.2. Calibration

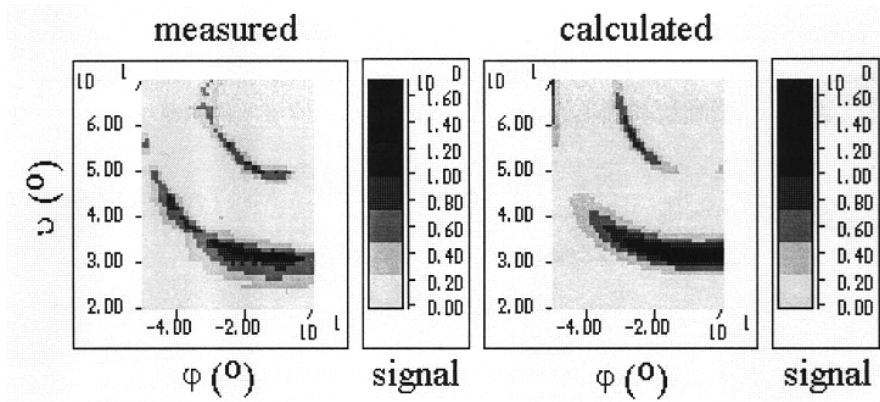
The system was calibrated in three ways: firstly, by measuring Maker fringes in  $\text{KH}_2\text{PO}_4$  with linear-polarized light, secondly with circularly polarized light and thirdly by measuring the SHG signal from a sphere of  $\text{KH}_2\text{PO}_4$ . The  $d$  coefficient of  $\text{KH}_2\text{PO}_4$  is  $d_{123} = -0.39 \text{ pm V}^{-1}$  (Veerabhadra and Narasimhamarty 1978, Craxton 1981). The refractive indices were taken from Zernicke (1964).

Figure 2 shows Maker fringes with polarized light in a  $\text{KH}_2\text{PO}_4$  crystal plate that had been cut along the optical axis. The sample was tilted so that the wavevector moved

towards [110]. The maximum angle between [001] and the wavevector was limited to about  $70^\circ$  by the cradle circles. No  $Q$  switch was used because the intensity of the signal was easily observed without it. The measurement was repeated with circularly polarized light, whereby the sample was remounted to test the reproducibility of the experiment. The theoretical description was fitted to both measurements with the known  $d_{123}$  of  $\text{KH}_2\text{PO}_4$  and an unknown factor  $K_{plate}$  to calibrate the sensitivity of the photomultiplier. The calibration procedure gave identical values for  $K_{plate}$  for linear- and circularly polarized light (figure 3). That we obtained an acceptable agreement between the experimental results and calculations confirmed the theoretical approach. However, using an additional optical component to produce circularly polarized light caused slightly larger errors in the peak heights, compared with the linear-polarized case. On the other hand, circularly polarized light has the advantage that the direction of the initial polarization need not be adjusted.



**Figure 4.** The dependence of the SHG signal on cradle angles  $\varphi$  and  $\nu$  in a sphere (of diameter 6.0(1) mm) of  $\text{KH}_2\text{PO}_4$  and the calculated spectrum.



**Figure 5.** The dependence of the SHG signal on cradle angles  $\varphi$  and  $\nu$  in a sphere (of diameter 4.8(1) mm) of mannitol and the calculated spectrum.

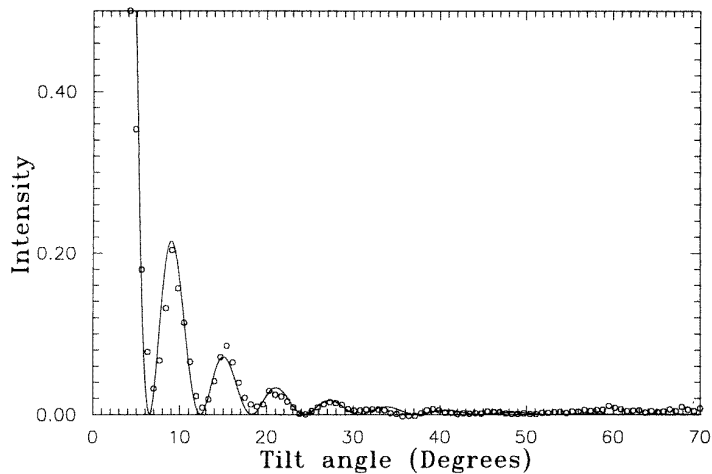
Circularly polarized light was also used on a sphere (diameter  $d = 6.0(1)$  mm) made from a  $\text{KH}_2\text{PO}_4$  crystal. The sphere was oriented by using Laue back-scattering photographs. Figure 4 shows the resulting signal, which was screened by the goniometer mount for larger values of  $\nu$  and  $\varphi$ . The calculation gave a different factor  $K_{\text{sphere}}$  which relates the theoretical description to the set-up resulting from the confocal refraction of the sphere and because the signal had to be attenuated with a 5%-transmission filter. The so-called half-width factors  $w$  (see section 2) were fitted to produce an acceptance angle of about  $4^\circ$  for spheres of about 5–6 mm diameter and refractive indices close to 1.5.

### 3.3. Measurements on mannitol

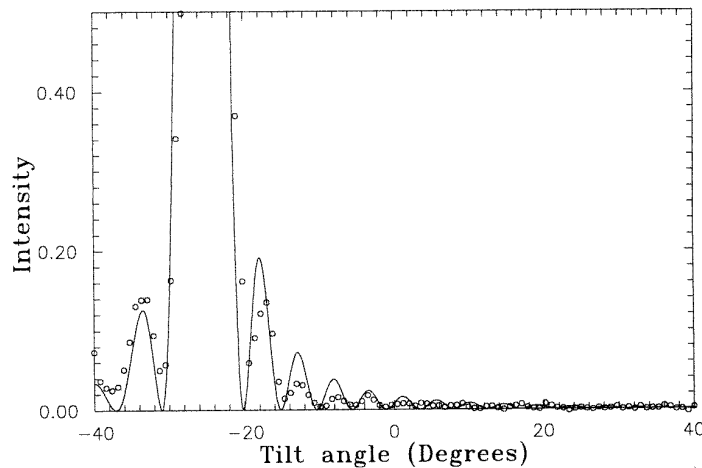
Figure 5 shows the SHG intensity collected from one quadrant of a sphere of mannitol of similar diameter to the  $\text{KH}_2\text{PO}_4$  sample. After we had adjusted the half-width factors and recalculated the calibration factor  $K_{\text{sphere}}$  to match the measurement with a 30%-transmission neutral density filter, the  $d$  coefficients were fitted with refractive indices from Kaminsky and Glazer (1997). As a result, the best fit was found for the  $d$  coefficients  $d_{123} = 0.08(2)$   $\text{pm V}^{-1}$ ,  $d_{231} = 0.07(2)$   $\text{pm V}^{-1}$  and  $d_{312} = 0.05(2)$   $\text{pm V}^{-1}$ . Kleinmann's rule was confirmed to within

the accuracy of the experiment. However, we estimate the error due to the calibration of the sphere to be about 20%.

To test the accuracy of the results, Maker fringes were collected on a mannitol plate, containing the axis  $c$  and cut at  $45^\circ$  towards  $a$  and  $b$  (figure 6). By chance, the normal to the plate was close to the direction of type II phase matching. Circularly polarized light was used. The result was fitted with an effective  $d$  coefficient of  $0.5(d_{231} + d_{123}) = 0.06(1)$   $\text{pm V}^{-1}$ . Because the signal along the phase-matching loci in the plates slightly exceeded the linear regime of the photomultiplier, intensities within a tilting angle of the plates of  $\pm 5^\circ$  of the phase-matching angle were omitted from the fitting procedure. Outside this range the intensities did not saturate the detector and so these measurements could be used to infer to reasonable precision the phase-matching loci. The measurements along the phase-matching loci for spheres were carried out in the linear response regime of the photomultiplier by attenuating the signal to 5% of its original value. Phase matching affected the measurement in a diagonal cut containing the  $a$  axis (figure 7) in a similar way to that in figure 6, but for the sake of retaining the weaker fringes we did not attenuate the signal further. Here, the best fit was obtained with  $0.5(d_{213} + d_{312}) = 0.06(2)$   $\text{pm V}^{-1}$ . From this it is very likely that  $d_{123} = d_{213} = d_{312} = 0.06(2)$   $\text{pm V}^{-1}$ .



**Figure 6.** Maker fringes with circularly polarized light of a mannitol sample plate containing  $c$  and cut  $45^\circ$  towards  $a$  and  $b$  ( $(1, 1, 0)^p$  of the physical reference system, see section 2.1:  $(1, 1, 1)^p \parallel [1/a \ 1/b \ 1/c]$  in mannitol). The thickness is  $0.470(5)$  mm. The quarter-wave plate was inserted at  $45^\circ$  inclined towards the linear initial polarization. The wavevector was tilted from  $(1, 1, 0)^p$  towards  $[010]$ .



**Figure 7.** Maker fringes of a mannitol-sample plate cut on  $(0, 1, 1)^p$  with circularly polarized light. The thickness is  $0.520(5)$  mm. The wavevector was tilted about  $(0, 1, 1)^p$  from  $[001]$  towards  $[010]$ .

## 4. Discussion

### 4.1. Experimental aspects

The numbers in table 1 show how errors of various origins affect the calibration and  $d$  coefficient determination. A calibration error of 20% is the minimum error achieved with crystal spheres. Further measurements using this calibration introduce additional errors, which produce the rather large error of 30% in the measured  $d$  coefficients from a mannitol sphere experiment. The calibration of plates is much more accurate and the  $d$  coefficients are more precisely measured in this way. However, the relative signs of the  $d$  coefficients are easily derived from spheres.

The measurements of mannitol in the form of a sphere and as plates, both calibrated against  $\text{KH}_2\text{PO}_4$ , were reasonably in accord in terms of the resulting  $d$  coefficients, to within 20%. The preparation of the spheres is more difficult than is that of the plates, but it was possible to improve the quality of the sphere surface with an index-

matching fluid. In the case of plates, it may be possible to coat the surfaces with a glass plate and an index-matching immersion fluid, but the use of additional optical components caused other problems. In addition, the larger acceptance angle in spheres made it easier to find the location of phase matchability and the quasi-independence of the surface reflections relative to the sphere's orientation simplified the calculations.

On the other hand, we needed rather large single crystals ( $7 \text{ mm} \times 7 \text{ mm} \times 7 \text{ mm}$ ), from which the spheres were prepared in order to achieve sufficient quality. An attempt to use smaller spheres made in an air-driven spherizer failed because they were ellipsoidal in shape and had a rather rough surface, both defects being a result of the cleavage face on  $(010)$  in mannitol. The measurements presented here were only performed on transparent spheres in which none of these defects were visible.

One general problem with spheres is that they are of use only for materials that exhibit phase matchability. In such a

**Table 1.** Details of the calibration and the measurements in KDP and mannitol. The refractive indices of KDP are  $n_o = 1.4950$  and  $n_e = 1.4605$  at 1064 nm and  $n_o = 1.5117$  and  $n_e = 1.4699$  at 532 nm (Zernicke 1964). The refractive indices of mannitol are  $n_1 = 1.5432$ ,  $n_2 = 1.5098$  and  $n_3 = 1.5499$  at 1064 nm and  $n_1 = 1.5554$ ,  $n_2 = 1.5216$ ,  $n_3 = 1.5615$  at 532 nm (Kaminsky and Glazer 1997).  $L$  is the thickness of crystal plates and  $d$  the diameter of spheres. The half-width factors  $w$  (type I) and  $w$  (type II) are numbers, which connect the line width of the Gaussian phase-matching profile in spheres to the coherence lengths of type I or type II phase matching, respectively (see the discussion of crystal spheres in section 2.2).  $\nu_0$  and  $\varphi_0$  are offsets of the cradle angles with which the adjustment of the samples is refined. The errors of the transmission filters are those due to the manufacturer. The factor  $K$  calibrates the photomultiplier:  $U(\text{photomultiplier}) = K I_{2\omega}(d_{ijk})$ , where  $I_{2\omega}(d_{ijk})$  is described in the appendix. If the sensitivity of the detector system is increased by a factor of six when replacing the 5%-transmission filter by a 30%-transmission filter, the calibration factor  $K$  has to be increased by a factor of six too. The orientation of the sample is specified with respect to the physical reference system  $(x, y, z)^p$  such that the unit-basis vectors are chosen along the crystallographic axes  $a$ ,  $b$  and  $c$  in mannitol. Thus a crystal plate cut at  $45^\circ$  to  $a$  and  $b$  is parallel to  $(1, 1, 0)^p \parallel [(1 a/b 0) \parallel (1 b/a 0)]$  in orthorhombic mannitol. The overall error is the sum of the errors of various sources and is a measure either of the total error of the calibration or of the error in the measurement of the  $d$  coefficient.

	KDP sphere	Mannitol sphere	KDP (001)	KDP (001)	Mannitol $(1, 1, 0)^p$	Mannitol $(0, 1, 1)^p$
Initial polarization	Circular	Circular	Linear	Circular	Circular	Circular
$L/d$ (mm)	$6.0 \pm 0.1$	$4.8 \pm 0.1$	$0.342 \pm 0.001$	$0.342 \pm 0.001$	$0.470 \pm 0.05$	$0.520 \pm 0.005$
$w$ (type I)	$3000 \pm 300$	$2500 \pm 300$				
$w$ (type II)	$1000 \pm 200$	$700 \pm 200$				
Transmission filter	$5 \pm 0.6\%$	$30 \pm 4\%$	None	None	None	None
Calibration constant $K$ (au)	$2400 \pm 300$	$K(\text{KDP}) \times 6$	$8500 \pm 500$	$10\,000 \pm 1000$	KDP circular	KDP circular
$\nu_0$ (degrees)	5	-7	3	0.8	1	-1.5
$\varphi_0$ (degrees)	3	-3				
$d$ coefficients ( $\text{pm V}^{-1}$ )	$d_{123} = -0.39$	$d_{123} = 0.08(2)$ $d_{231} = 0.07(2)$ $d_{312} = 0.05(2)$	$d(\text{KDP})$	$d(\text{KDP})$	$1/2(d_{231} + d_{123}) = 0.06(1)$	$1/2(d_{213} + d_{312}) = 0.06(2)$
Overall error	Calibration 20%	$d$ coefficient 30%	Calibration 7%	Calibration 10%	$d$ coefficient 15%	$d$ coefficient 20%

case, spheres provide larger signals of the integrated SHG-peak signal than do plates, for which the slightest defects of the sample diminish the height of the SHG-matching peaks drastically. Therefore these directions are usually avoided in Maker fringe experiments. Larger signals allow measurements with less intense initial light. For a large number of crystals which decay rapidly if bombarded with strong  $Q$ -switched infra-red pulses use of spheres may be the only way to find the  $d$  coefficients.

Another weakness of spheres is that signals can be observed in directions where SHG in theory is not possible. These result from multiple reflections inside the sphere and the conical refraction which brings deflected parts of the initial beam into a phase-matching position (see figure 4, type I phase matching in  $\text{KH}_2\text{PO}_4$  for  $\varphi = 0$  and  $\nu \simeq 45^\circ$ ). Although these forbidden signals are small, they clearly indicate that there are limits to the accuracy of the  $d$  coefficients determined with spheres.

#### 4.2. Model calculations

The figure of merit ( $d^2 n^{-3}$ ) of mannitol,  $0.0013 \text{ pm}^2 \text{ V}^{-2}$ , is much smaller than that of  $\text{KH}_2\text{PO}_4$ ,  $0.045 \text{ pm}^2 \text{ V}^{-2}$ . Therefore this investigation has only academic value, which is to test the method and the model calculations.

From the DES model (table 2), a totally symmetrical  $d$  tensor was originally calculated with  $d_{123} = 0.21 \text{ pm V}^{-1}$ . This is much larger than that observed ( $d_{123}^{\text{measured}} = 0.06(2) \text{ pm V}^{-1}$ ). However, the calculation was based on the polarizabilities  $\alpha$  derived from a fit of

calculated refractive indices to the experimental refractive indices. In using both oxygens and carbons in the model, a quite high polarizability for the carbons ( $0.2 \text{ \AA}^3$ ) resulted from the best fit ( $\alpha$  oxygen =  $1.9 \text{ \AA}^3$ ) to the refractive indices. Thus, the  $d$  coefficients were calculated semi-empirically, using only the crystal structure and the refractive indices of mannitol. As has been described by Kaminsky and Glazer (1997), there was a strong correlation between the polarizabilities of oxygen and carbon and almost no difference in the calculated refractive indices was observed if the polarizability of carbon was set to the more realistic, but still high, value of  $0.05 \text{ \AA}^3$  and only the polarizability of oxygen was allowed to be adjusted. Although the calculated refractive indices and optical gyration were almost independent of the changed carbon polarizability, the induced effects were calculated to be much smaller. As a result, we found  $\alpha$  oxygen (modelled) =  $2.27 \text{ \AA}^3$  and  $d_{123}^{\text{calc}} = 0.075 \text{ pm V}^{-1}$ . An even smaller value for the carbons resulted in too large a deviation of the calculated optical activity from the experimental values. The accord between calculation and experiment is thus improved. With the new set of polarizabilities, which are still well within the accepted range of values found in the literature, we also find better agreement between calculated and measured electro-optical coefficients for mannitol:  $r_{123/231/312}^{\text{exp}} = -0.23$ ,  $-0.2$  and  $-0.16 \text{ pm V}^{-1}$  for  $r_{123/231/312}^{\text{calc}} = -0.2$ ,  $-0.25$  and  $-0.25 \text{ pm V}^{-1}$ .

**Table 2.** A comparison of measured  $d$  coefficients ( $\text{pm V}^{-1}$ ) and those calculated with the DES model for some substances.  $\alpha$  is the polarizability volume ( $\text{\AA}^3$ ). The modelled polarizabilities, which were obtained from fitting the calculated refractive indices to the experimental values, have to be compared with those given by Tessman *et al* (1953). References to structures are 1, Landolt–Börnstein (1969); 2, le Page (1976); and 3, Kaminsky and Glazer (1996). References to experimental  $d$  coefficients are a, Craxton (1981) and Veerabhadra *et al* (1978); b, Jerphagnon and Kurtz (1970) and Miller and Nordlund (1970); and c, this paper.

Substance	Structure	Experimental	Reference	$\alpha$ (Tessman <i>et al</i> )	$\alpha$ model	Calculation
$\text{KH}_2\text{PO}_4$	1	$d_{123} = -0.39$	a	O: 1.8 K: 1	O: 1.206 K: 0.642 P: 0.396	$d_{123} = -0.56$
$\text{SiO}_2$	2	$d_{111} = -0.25$ $d_{123} = 0.007$	b	O: 1.8 Si: 0.04	O: 1.903 Si: 0.2308	$d_{111} = -0.26$ $d_{123} = 0.044$
$\text{C}_6\text{H}_{14}\text{O}_6$	3	$d_{123} = 0.06(2)$	c	O: 1.8 C: 0.01	O: 2.27 C: 0.05	$d_{123} = 0.075$

### 4.3. Final conclusions

The theory needed for measurements using crystal spheres has been outlined. When materials such as mannitol and  $\text{KH}_2\text{PO}_4$  have directions that allow one to establish phase matching, measurement of the SHG efficiency can be performed in order to find the  $d$  coefficients and phase-matching loci. The accuracy of such determinations of  $d$  coefficients should not be expected to be better than 20%.

Although it is possible to observe a stronger SHG signal with spheres than it is with crystal plates, the great difficulty in preparing a sphere most probably acts against its routine use in the laboratory. The DES model, which describes well the  $d$  coefficients of  $\text{KH}_2\text{PO}_4$  and  $\alpha$ - $\text{SiO}_2$ , predicted a rather small SHG efficiency in mannitol. This result was confirmed by experiment. Thus the DES model may be useful in classifying non-linear materials ahead of time. However, a further comparison of calculation and measurement is needed in order to establish the reliability of the DES model in general and especially for organic compounds.

### Appendix

The following describes briefly the equations involved in relating the  $d$  coefficients to the experimental evidence. The tensor  $d_{ijk}$  ( $d$  coefficients) connects the induced electrical polarization  $\mathbf{P}$  to the applied electric field vector  $\mathbf{E}$  of the light wave:

$$P_i(2\omega) = \varepsilon_0 d_{ijk} E(\omega)_j E(\omega)_k$$

(Kurtz 1975, Boyd and Kleinmann 1968, Ward and New 1968). For small  $d$  coefficients, it follows from the exact treatment of the intensity that  $I(2\omega)$  generated by  $I(\omega)$ ,  $\omega$  is the circular velocity, is given by (Armstrong *et al* 1962)

$$I_{2\omega} = \frac{2\omega^2}{\varepsilon_0 c^3} \frac{d_{eff}^2}{n'_{2\omega} n''_{2\omega}} L^2 I_{\omega}^2 \frac{\sin^2 x}{x^2}$$

$$x = L \frac{\omega}{c} (n'_{\omega} - n'_{2\omega}) \quad (\text{type I})$$

$$x = L \frac{\omega}{2c} (n'_{\omega} + n''_{\omega} - 2n'_{2\omega}) \quad (\text{type II})$$

where only those differences of refractive indices are included which promise phase matchability (normal dispersion and  $n'' > n'$ ). The dash and double-dash are used to distinguish between the two allowed vibration modes  $E'_{\omega}$ ,  $E''_{\omega}$  and  $E'_{2\omega}$ ,  $E''_{2\omega}$  normal to the wavevector  $\mathbf{k}$ . The effective  $d$  coefficient is given by

$$d_{eff} = \frac{d_{ijk} E'_i(2\omega) E'_j(\omega) E'_k(\omega)}{E''^2(\omega) E'(2\omega)} \quad (\text{type I})$$

$$d_{eff} = \frac{d_{ijk} E'_i(2\omega) (E'_j(\omega) E''_k(\omega) + E''_j(\omega) E'_k(\omega))}{2E'(\omega) E''(\omega) E'(2\omega)} \quad (\text{type II})$$

where  $L$  is the sample thickness and  $c$  is the velocity of light in a vacuum. If the unit vector  $\mathbf{s}^0$  denotes the direction of the wavevector with respect to the optical reference system  $\mathbf{e}_i^0$  and if we assume that the  $\mathbf{k}$  vectors of incident and emerging waves are both approximately parallel to  $\mathbf{s}^0$ , the directions of the  $\mathbf{E}$  vectors are found from

$$E_i \propto \frac{s_i^0}{n^2 - n_i^2}$$

where  $n_i$  are the principal refractive indices of the indicatrix. In monoclinic and triclinic crystals the  $\mathbf{E}$  vectors have to be transformed with respect to the reference system of the indicatrix according to  $\mathbf{e}_i^0 = v_{ij} \mathbf{e}_j$  with  $\mathbf{s}_i^0 = v_{ij} s_j$ , from which it follows that  $E_i^{phys} = v_{ij}^{-1} E_j^{optic}$ . Here  $\mathbf{s}$  is the wavevector with respect to the physical reference system  $\{\mathbf{e}_i\}$ .

The problem now lies in calculating the set of refractive indices  $n'$ ,  $n''(\omega)$ ,  $n'$ ,  $n''(2\omega)$  which have to be substituted for  $n$  in the equation above. Use is made of the Fresnel equation

$$\frac{s_i^0}{n_i^{-2} - n^{-2}} s_i^0 = 0$$

which can be written as  $n^4 - Bn^2 + C = 0$ ;

$$B = \sum_i s_i^{02} (n_j^{-2} + n_k^{-2}) \quad C = \sum_i s_i^{02} n_j^{-2} n_k^{-2}$$

$i, j, k$  cyclic 1, 2, 3

and finally (Yao and Fahlen 1984)

$$n'(n'') = \frac{\sqrt{2}}{[B + (-)(B^2 - 4C)^{1/2}]^{1/2}}$$



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