

## Elastic Constants of Orthorhombic KNbO<sub>3</sub> by X-ray Diffuse Scattering

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(Received 8 March 1971)

All nine elastic constants of orthorhombic potassium niobate (space group *Bmm2*) have been determined at room temperature from a diffractometric study of 006, 040 and 600 diffuse reflexions. The values of the elastic constants in units of 10<sup>12</sup> dynes.cm<sup>-2</sup> are:

$$\begin{aligned} C_{11} &= 0.354, & C_{22} &= 0.516, & C_{33} &= 0.632, \\ C_{44} &= 3.558, & C_{55} &= 3.651, & C_{66} &= 2.069, \\ C_{12} &= -1.058, & C_{23} &= -1.914, & C_{13} &= -2.027. \end{aligned}$$

Equiscattering contours and *K* surfaces have been calculated using these values of the elastic constants.

### Introduction

Potassium niobate (KNbO<sub>3</sub>) is isomorphous with the much studied barium titanate (BaTiO<sub>3</sub>) (see *e.g.* Jona & Shirane, 1962). KNbO<sub>3</sub> is orthorhombic (space group *Bmm2*) at room temperature; it becomes tetragonal at 230°C and cubic at 435°C. The high Curie point (435°C) makes KNbO<sub>3</sub> a potentially useful ferroelectric. The crystal structure of orthorhombic KNbO<sub>3</sub> has been studied in detail by Katz & Megaw (1967) and Dwivedi & Srivastava (private communication, 1969). The pertinent crystal data are summarized in Table 1. Although the dielectric and thermal properties of KNbO<sub>3</sub> have been studied in considerable detail (Jona & Shirane, 1962), no information on the elastic constants is available. In the present investigation all the nine (six independent and three dependent) elastic constants of orthorhombic KNbO<sub>3</sub> have been determined by a study of X-ray diffuse reflexions from selected planes. With this method, only small single-domain single-crystals are needed, so it is more suitable than other methods where large and oriented single crystals are necessary.

Table 1. Crystal data on potassium niobate

Chemical formula	KNbO <sub>3</sub>
Crystal class	Orthorhombic ( <i>mm2</i> )
Axial parameters	<i>a</i> 5.697 Å <i>b</i> 3.971 <i>c</i> 5.721
Space group	<i>Bmm2</i>
Number of molecules per unit cell	2
Volume of the unit cell	129.425 Å <sup>3</sup>
*Measured density	4.62 g.cm <sup>-3</sup>
*Linear absorption coefficient ( $\mu_c$ ) of KNbO <sub>3</sub> for Mo <i>K</i> $\alpha$ radiation:	
$\mu_c$ (calculated)	58.21 cm <sup>-1</sup>
$\mu_c$ (observed by diffractometer method)	55.93

\* Present study. Remaining data taken from Katz & Megaw (1967).

The ratio ( $\sigma$ ) of the intensity of first-order diffuse X-ray reflexions  $I_d$  (per unit cell) to that of the incident beam  $I_0$ , corresponding to a particular thermal wave vector  $\mathbf{q}$  (where  $\mathbf{q} \rightarrow 0$ ) and the reciprocal lattice point  $hkl$  is given by the following expression (Ramachandran & Wooster, 1951):

$$\sigma = \frac{I_d}{I_0} = \frac{\epsilon^2 k T \Omega}{2 \mu_c V^2} F_T^2 \frac{|\mathbf{X}^2|}{|\mathbf{q}|^2} K [uvw]_{hkl}, \quad (1)$$

where

$k$  = Boltzmann constant.

$T$  = absolute temperature at which observations are made.

$\Omega$  = solid angle subtended at the crystal by the counter collimator slit.

$I_0$  = incident (direct) beam intensity.

$F_T$  = structure factor of the reflexion  $hkl$  at temperature  $T$ .

$\mathbf{X}$  = reciprocal lattice vector corresponding to  $hkl$ .

$V$  = volume of the unit cell.

$\mathbf{q}$  = thermal wave vector.

$\mu_c$  = linear absorption coefficient of the crystal.

$\epsilon$  = amplitude of scattering by a classical electron, given by the well-known formula:

$$\epsilon = \frac{e^2}{mc^2} (A^2 + B^2 \cos^2 \varphi)^{1/2},$$

where  $m$  and  $e$  are the mass and charge of the electron,  $c$  the velocity of light,  $\varphi$  the angle through which the X-rays have been deviated due to scattering, and  $A$  and  $B$  the amplitude components of the incident intensity ( $I_0$ ), normal and parallel, respectively, to the plane of incidence.  $K[uvw]_{hkl}$  is given by:

$$\begin{aligned} K[uvw]_{hkl} &= L^2 A_{11}^{-1} + M^2 A_{22}^{-1} + N^2 A_{33}^{-1} \\ &\quad + 2MNA_{23}^{-1} + 2NLA_{13}^{-1} + 2MLA_{12}^{-1}, \quad (2) \end{aligned}$$

where  $L, M, N$  and  $u, v, w$  are the direction cosines of  $\mathbf{X}$  and  $\mathbf{q}$  respectively, with reference to the orthogonal elastic axes.  $A_{ij}^{-1}$  are the elements of the matrix  $A_{ij}^{-1}$ , which is inverse to the matrix  $A_{ij}$  where  $i$  and  $j$  have

values 1,2 and 3. The elements  $A_{ij}$  are given by the following matrix equation:

$$\begin{bmatrix} A_{11} \\ A_{22} \\ A_{33} \\ A_{23} \\ A_{13} \\ A_{12} \end{bmatrix} = \begin{bmatrix} C_{11} & C_{66} & C_{55} & C_{56} & C_{15} & C_{16} \\ C_{66} & C_{22} & C_{44} & C_{24} & C_{46} & C_{26} \\ C_{55} & C_{44} & C_{33} & C_{43} & C_{35} & C_{45} \\ C_{56} & C_{24} & C_{34} & \frac{1}{2}(C_{23} + C_{44}) & \frac{1}{2}(C_{45} + C_{36}) & \frac{1}{2}(C_{46} + C_{23}) \\ C_{15} & C_{46} & C_{35} & \frac{1}{2}(C_{45} + C_{36}) & \frac{1}{2}(C_{13} + C_{55}) & \frac{1}{2}(C_{65} + C_{14}) \\ C_{16} & C_{26} & C_{45} & \frac{1}{2}(C_{64} + C_{25}) & \frac{1}{2}(C_{56} + C_{14}) & \frac{1}{2}(C_{12} + C_{66}) \end{bmatrix} \begin{bmatrix} u^2 \\ v^2 \\ w^2 \\ 2uw \\ 2vw \\ 2uw \end{bmatrix}. \quad (3)$$

The elastic matrix  $C_{ij}$  on the right-hand side of equation (3) reduces to a simplified form given below for crystal class  $mm2$  (Bhagavantam, 1966).

$$\begin{matrix} C_{11} & C_{12} & C_{13} & 0 & 0 & 0 \\ & C_{22} & C_{23} & 0 & 0 & 0 \\ & & C_{33} & 0 & 0 & 0 \\ & & & C_{44} & 0 & 0 \\ & & & & C_{55} & 0 \\ & & & & & C_{66} \end{matrix} \quad (4)$$

The constants  $K[uvw]_{hkl}$  have a simple relationship (Table 2) with the elastic constants for simple planes (e.g.  $h00$ ) and particular directions of propagation of the thermal wave. In principle, therefore, it is possible to compute the elastic constants from the experimentally determined values of  $K[uvw]_{hkl}$ .

Table 2. Elastic constant values and the thermal wave propagation directions ( $K[uvw]_{hkl}$ )

K direction	Elastic constant	Elastic constants $\times 10^{-12}$ dynes. $\text{cm}^{-2}$	
		After first-order correction	After second-order correction
$K[100]_{600}$	$C_{11}$	0.329	0.354
$K[010]_{040}$	$C_{22}$	0.486	0.516
$K[001]_{006}$	$C_{33}$	0.608	0.632
$K[001]_{040}$	$C_{44}$	3.548	3.558
$K[100]_{006}$	$C_{55}$	3.609	3.651
$K[010]_{600}$	$C_{66}$	2.047	2.069
$K[\pm 1/\sqrt{2}, \pm 1/\sqrt{2}, 0]_{600}$	$C_{12}$	-1.069	-1.058
$K[0, \pm 1/\sqrt{2}, \pm 1/\sqrt{2}]_{040}$	$C_{23}$	-1.854	-1.914
$K[\pm 1/\sqrt{2}, 0, \pm 1/\sqrt{2}]_{006}$	$C_{13}$	-2.20	-2.027

This method was first successfully applied for the determination of elastic constants of cubic crystals by Ramachandran & Wooster (1951) and was later extended to non-cubic crystals by Prince & Wooster (1953) and Prasad & Wooster (1955, 1956). A detailed account of the method applied to molecular crystals is given by Amoros & Amoros (1968). The crystallogra-

phic data (Tables 1 & 3) for  $\text{KNbO}_3$  have been taken from Katz & Megaw (1967).

Table 3. Structure-factor data for planes studied

Plane studied	Axis of rotation	Structure factor $ F_T $	Reciprocal lattice vector X ( $\times 10^{-8}\text{cm}^{-1}$ )	Volume of the crystal ( $\times 10^3\text{cm}^3$ )
040	[100]	62.83†	1.0072	1.838
600	[001]	41.44	1.053	1.838
006	[010]	38.77	1.049	1.750
400	[010]	72.73	0.702	0.1782
004	[010]	71.92	0.699	0.1782
*400	[010]	71.92	0.699	0.0997

\* Studied photographically

† The  $|F_T|_{040}$  was taken from Dwivedi & Srivastava (private communication, 1969). The remaining  $|F_T|$  values were from Katz & Megaw (1967).

## Experimental

Small crystals of  $\text{KNbO}_3$  were produced from binary melts ( $\text{K}_2\text{CO}_3$  and  $\text{Nb}_2\text{O}_5$ ) using excess of  $\text{K}_2\text{CO}_3$  as a flux (Wood, 1951). Larger crystals were grown by the technique described by Miller (1958). These crystals are parallelepipedal in shape, with well-developed faces, and have a preferred cleavage perpendicular to the [010] axis. Crystals of approximately  $10^{-3}\text{cm}^3$  (which

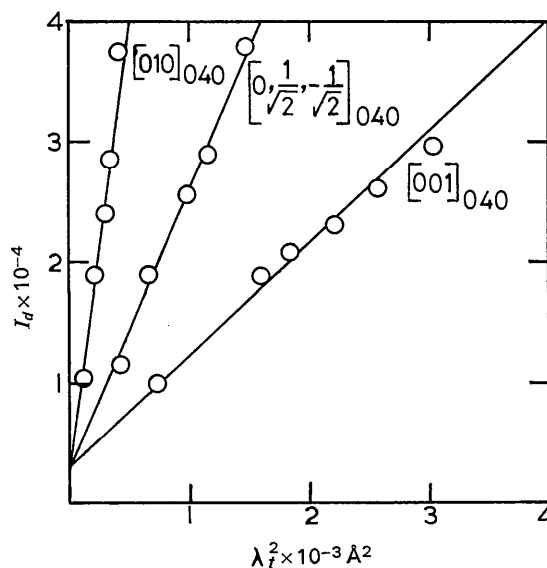


Fig. 1. Variation of diffuse intensity ( $I_d$ ) with the square of the wavelength ( $\lambda_i$ ) of the elastic wave for the 040 reflexion.

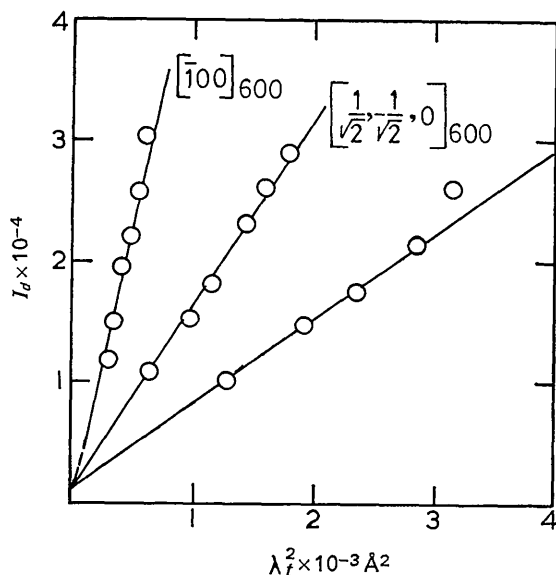


Fig. 2. Variation of diffuse intensity ( $I_d$ ) with the square of the wavelength ( $\lambda_l$ ) of the elastic wave for the 600 reflexion.

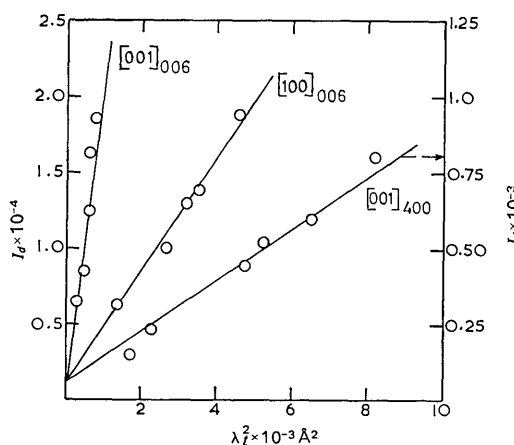


Fig. 3. Variation of diffuse intensity ( $I_d$ ) with the square of the wavelength ( $\lambda_l$ ) of the elastic wave for the 006 and 400 reflexions.

could be fully immersed in the X-ray beam) were annealed at about 800°C and examined by Laue photographs and polarizing microscope for any strains or the presence of multidomains. Crystals free from defects were chosen for the study.

Using the criteria discussed in detail by Ramachandran & Wooster (1951), reflexions 006, 600, and 040 with [010], [001] and [100] axes respectively vertically perpendicular to the incident X-rays were selected for the present study. On combining equations (2), (3) and (4), the elastic constants  $C_{11}$ ,  $C_{22}$ ,  $C_{33}$ ,  $C_{44}$ ,  $C_{55}$  and  $C_{66}$  can be determined independently from  $K[uvw]_{hkl}$  values (Prasad & Wooster, 1955). The remaining constants,  $C_{12}$ ,  $C_{23}$  and  $C_{13}$  can be derived from the

$K[uvw]_{hkl}$  values in specified directions (e.g.  $[\frac{1}{2}, 0, \frac{1}{2}]$ ) and the independent constants  $C_{11}$ , etc. (Table 2).

A G.E. XRD-6 diffractometer, with a single-crystal orienter, and Mo  $K\alpha$  radiation set employed for the study. To avoid higher harmonics ( $\lambda/2$ ,  $\lambda/3$ , etc.) of Mo  $K\alpha$ , the X-ray tube was operated at 35 kV and 25mA. The incident beam was monochromated by the method of balanced filters (Ross, 1928; Tanaka, Katayama, Chikawa & Suita, 1959; Burbank, 1965; Arndt & Willis, 1966).  $Y_2O_3$  pellets of appropriate thicknesses were prepared from spectroscopically pure  $Y_2O_3$  powder, so as to match precisely the Zr foils.

Observations at different mis-settings from the Bragg position were made and the time for 10,000 counts was recorded at each observation.  $I_0$ , the direct beam intensity, was measured by using the Compton scattering from diamond as an intermediate standard. The Compton Scattering around the 220 reciprocal lattice point was measured following the method of Prince & Wooster (1953) and Amoros & Amoros (1968). Diamond has been preferred to other substances commonly used, e.g. paraffin wax, because the coherent scattering from diamond is negligible except very close to reciprocal lattice points.

The linear absorption coefficient,  $\mu_c$ , of the  $KNbO_3$  crystal was determined by the diffractometer method using a scintillation counter (for better accuracy) and a balanced pair of Zr- $Y_2O_3$  filters. The value of  $\mu_c$  obtained experimentally ( $55.93 \text{ cm}^{-1}$ ) is in fair agreement with the theoretically calculated value of  $58.20 \text{ cm}^{-1}$ .

The observed diffuse intensity ( $I_d$ ) corresponding to a particular thermal wave vector was corrected for general scattering or background, skew, polarization, divergence, mosaic and white radiation, as described by earlier workers (Ramachandran & Wooster, 1951; Wooster, 1962; Amoros & Amoros, 1968). The absorption correction was applied following the method of Albrecht (1939). The correction due to second-order diffuse scattering was made in all cases by the method of successive approximation (Ramachandran & Wooster, 1951; Lucas, 1968, 1969, 1970).

For each reflexion, the intensity of diffuse reflexion ( $I_d$ ), after the corrections mentioned earlier had been made (except general and second-order diffuse scattering), was plotted against the square of the wave length of the corresponding thermal wave ( $\lambda_l = 1/q$ ) (Figs. 1, 2 & 3). It is evident from equation (1) that the plot of  $I_d$  versus  $\lambda_l^2$  for a particular reciprocal lattice point and the direction of propagation of the thermal wave should be a straight line passing through the origin (if background is subtracted from  $I_d$ ). Since the slope of the straight line gives  $I_d \times |q|^2$ , and other quantities in equation (1) are known,  $K[uvw]_{hkl}$  can be calculated. The relationship between the  $K$ 's corresponding to a particular direction of propagation of the thermal wave and the elastic constants is given in Table 2. All the nine elastic constants of  $KNbO_3$ , thus evaluated, are listed in the same table.

Two additional experiments were carried out to check the consistency of the results. In one, a crystal ten times smaller (*i.e.* volume  $\approx 10^{-4} \text{ cm}^3$ ) than the one on which most of the data were collected was selected and used to determine  $K[001]_{400}$  on a diffractometer. In the second experiment, the 400 diffuse reflexion was studied photographically with the  $[010]$  axis vertical as described by Chakraborty (1958), Chakraborty & Sen (1958) and Srivastava & Chakraborty (1962). In the photographic method, the  $\text{Mo K}\alpha$  radiation, reflected by a  $(200)$  plane of  $\text{LiF}$  crystal, was used; the X-ray tube was operated at 35 kV and 25 mA. The corrections applied to the diffuse intensity are similar for the diffractometer and the photographic methods, since the crystal was totally immersed in the X-ray beam in both cases. The results of these two experiments were compared with the values obtained on the larger crystal in Table 4. It may be concluded that (a) the size of the crystal for the diffractometer work need not be any larger than for the photographic technique, and (b) even for small crystals, the more convenient and faster diffractometer method is at least as good as the photographic method. These facts are particularly significant in the case of ferroelectrics where it is extremely difficult to obtain large single-domain single crystals (Phatak, 1970).

Table 4. Comparison of  $C_{55}$  values

Reflexion studied	Volume of the crystal ( $\times 10^4 \text{ cm}^3$ )	$C_{55}$ value obtained ( $\times 10^{-12}$ dynes. $\text{cm}^{-2}$ )	Technique
400	1.782	3.463	Diffractometer
400	0.997	3.497	Photographic
006	17.50	3.651	Diffractometer

### Results and discussion

The accuracy of the determination of the elastic constants is primarily dependent on the accuracy of the determination of  $I_d/I_0$ . It is, therefore, necessary to account for the various correction factors, *e.g.* divergence and absorption, mentioned earlier. The computational details of applying these corrections have been described in detail elsewhere (Phatak, 1970). The constants  $C_{11}$ ,  $C_{22}$ ,  $C_{33}$ ,  $C_{44}$ ,  $C_{55}$  and  $C_{66}$  which depend on single  $K[uvw]_{hkl}$  values are estimated to be accurate to within  $\pm 8\%$ , whereas the accuracy of  $C_{12}$ ,  $C_{13}$ , and  $C_{23}$  which depend on two  $K$ 's is estimated to be  $\pm 12\%$ .

#### Equiscattering contours

These are surfaces surrounding each reciprocal lattice point over which the diffuse intensity has a constant value (also called the surfaces of equidiffusion). The equiscattering contours for reciprocal lattice points 400 and 600 were calculated following the method of Jahn (1942) and were plotted in reciprocal planes  $a^*c^*$  and  $a^*b^*$  [Fig. 4(a) & (b)]. The equiscattering contour around node 400 [Fig. 4(a)] shows that for this particular crystal the thermal wave vector

$|\mathbf{q}|_{100} > |\mathbf{q}|_{001}$ . Similarly, the equiscattering contour around node 600 [Fig. 4(b)] shows  $|\mathbf{q}|_{100} > |\mathbf{q}|_{010}$ . These inequalities are implicit in the values of elastic constants requiring that  $C_{55} > C_{11}$  and  $C_{66} > C_{11}$  respectively (Table 2).

#### $K$ -surfaces

The intensity of the diffuse reflexions from a reciprocal lattice point varies markedly with the direction, and this directional dependence is implied in the expression for  $K[uvw]_{hkl}$  [equation (2)]. The variation of diffuse scattering can be conveniently expressed by means of surfaces of constant  $K$ . The equiscattering contour is only a particular case of  $K$  surface.

The projections of  $K$  surfaces for the reciprocal lattice points 600 and 006 on  $[001]$  and  $[010]$  respectively were

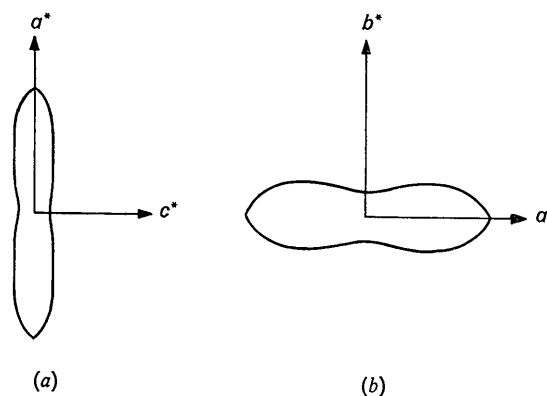


Fig. 4. Equiscattering contours (a) around 400 in the  $a^*c^*$  reciprocal plane, (b) around 600 in the  $a^*b^*$  reciprocal plane.

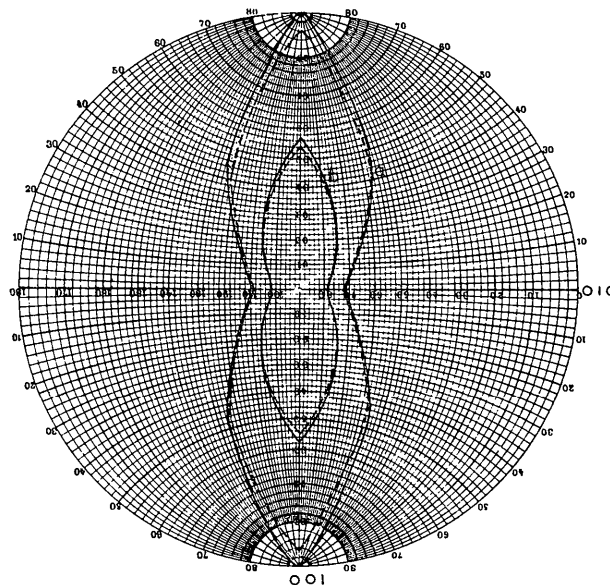


Fig. 5. Stereographic projection of the  $K$  surface for  $\text{KNbO}_3$ ; (a) reflexion 600 projected on  $[001]$  and (b) reflexion 006 projected on  $[010]$ .

calculated using the experimentally determined elastic constants and are shown in Fig. 5 where the dotted curves are corrected for second-order diffuse reflexion and the solid curves are without this correction. The variation of second-order correction with direction can be seen from Fig. 5.

The authors are grateful to Professor B. K. Agarwal and Dr L. P. Verma of Allahabad University for assistance in the microdensitometer records of the photographs.

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*Acta Cryst.* (1972). **A28**, 231

## Absorption and Volume Corrections for a Cylindrical Specimen, Larger than the Beam, and in General Orientation

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(Received 21 April 1971)

A theory and a computer procedure are developed by which both the absorption and the volume corrections for a cylindrical sample of infinite length, larger than the beam, enclosed in a concentric cylindrical tube, and in general orientation in the Eulerian cradle, can be carried out. The combined corrections can be used in the simpler case of an exposed sample. Moreover, the absorption correction can be applied to the case of a cylindrical window, such as may be employed in low-temperature studies, surrounding a sample of conventional size.

A theory for both the absorption and volume corrections for a cylindrical specimen, larger than the beam, and whose axis is coincident with the  $\varphi$ -axis of the goniometer, is given in an earlier paper (Coyle & Schroeder, 1971). In the present paper, an extension of that theory is developed for the case of a similar specimen, but in general orientation. The two corrections for such a crystal are available as computer program *CYCAC*.

The same terminology and symbols are followed here, but additional independent angles are defined for the sake of convenience and in such a way as to obtain equations algebraically symmetrical to those of the earlier paper.

Let  $\Gamma$ , where  $0 \leq \Gamma \leq \pi/2$ , be the angle between the crystal axis  $J$  and the  $\varphi$  axis of the diffractometer. If  $\Gamma$  is less than, or equal to, the maximum possible arc settings (the usual case), it is given by  $\cos \Gamma = \cos \gamma_i \cos \gamma_o$ , where  $\gamma_i$  and  $\gamma_o$  are the inner and outer arc setting differences required to bring the two axes into coincidence.

Furthermore, let the  $\chi$  circle be a great circle of a

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