

Polymorphism and Disordered Structures of *o*-Chlorobenzamide*

BY YOSHIHIRO KATO, YOSHITO TAKAKI AND KIICHI SAKURAI

Department of Physics, Osaka Kyoiku University, Tennoji, Osaka 543, Japan

(Received 14 January 1974; accepted 30 June 1974)

The crystal structures of two polymorphs of *o*-chlorobenzamide, α and β , have been determined from three-dimensional X-ray data. The α form is monoclinic, space group $P2_1/n$, with $a = 14.127$, $b = 10.683$, $c = 5.051$ Å, $\beta = 90.2^\circ$, $Z = 4$. The β form is orthorhombic, space group $P2_12_12_1$, with $a = 14.030$, $b = 10.599$, $c = 5.064$ Å, $Z = 4$. Both structures are described in terms of stacking of molecular layers in which the molecules are arranged almost identically. Between the layers, molecules are connected by $\text{NH}\cdots\text{O}$ hydrogen bonds, to form in the α form, dimers, and, in the β form, a staggered chain parallel to c . The polymorphism is found to be caused by different modes of stacking of layers. Two additional polymorphs, γ and δ , were obtained. Their structures show one-dimensional disorder and are closely related to those of the α and β forms.

Introduction

The crystal structure of *o*-chlorobenzamide, $\text{C}_7\text{H}_6\text{NOCl}$, has been investigated as part of our study on the crystal structures of monohalogenobenzamides.

The structures of *m*- and *p*-fluorobenzamide (Taniguchi, Kato, Takaki & Sakata, 1965; Takaki, Taniguchi & Sakurai, 1965), *p*-chlorobenzamide (Harada, Taniguchi, Takaki & Sakurai, 1969), *o*-, *m*- and *p*-bromobenzamide (Izumi & Okamoto, 1972; Kato, Taniguchi, Takaki & Sakata, 1967; Harada, Taniguchi, Takaki & Sakurai, 1967) and *p*-iodobenzamide (Nakata, Kato, Takaki & Sakurai, 1971) have already been determined from two-dimensional X-ray data.

The molecules so far found in the crystals of monohalogenobenzamides are connected by one type of $\text{NH}\cdots\text{O}$ hydrogen bond to form dimers, which are linked into one-dimensional chains or two-dimensional networks by the other type of $\text{NH}\cdots\text{O}$ hydrogen bond.

The main purpose of the present investigation is to determine the molecular configuration and the type of hydrogen bonding and to compare them with those of the above-mentioned crystals.

Two polymorphic forms, α and β , have been obtained. In addition, two forms showing one-dimensional disorder, γ and δ , have been found.

The present paper describes detailed three-dimensional structure analyses of the α and β forms. A brief account is given of the structures of the γ and δ forms and the structural relationships between these four polymorphs.

Experimental and crystal data

Single crystals of the α and β forms were obtained from aqueous solutions. They are colourless and elongated

along c . Crystals of the α form were also obtained by cooling the melt. Regarding the α form, crystals obtained by both methods were always hybrids containing a few per cent of the γ form. The data collection for the α form was carried out with a crystal as free from the γ form as possible. The cross-sections of the crystals used were 0.3×0.3 mm and 0.35×0.35 mm for the α and β forms. With filtered $\text{Cu } K\alpha$ radiation, multiple-film Weissenberg photographs were taken about \mathbf{b} ($k=0$), \mathbf{c} ($l=0\sim 5$) for the α and β forms, \mathbf{a} ($h=0$), \mathbf{b} ($k=0$), \mathbf{c} ($l=0$) for the γ form and \mathbf{b} ($k=0$) for the δ form. On the Weissenberg photographs of the γ and δ forms marked diffuse streaks parallel to \mathbf{a}^* were observed. An interpretation of this feature could be given by subsequent structure analyses of the α and β forms.

Crystals of the γ and δ forms were obtained accidentally, but later attempts to obtain these two forms were unsuccessful.

The lattice constants of the α and β forms were determined from photographs taken with a Buerger's back-reflexion Weissenberg camera, whose camera constant was calibrated by using Ag as a standard. Bragg reflexions from the γ form could be identified on the photograph about \mathbf{b} of the α form, and from these reflexions the lattice constants, a , c , β of the γ form were determined. Since only one set of Weissenberg photographs ($k=0$) was available, the lattice constants of the δ form, apart from β ($=90.0^\circ$), could not be determined precisely.

The crystal data of the four forms are listed in Table 1. It is remarkable that the unit-cell dimensions of the α and β forms agree within 0.8%.

Intensities of 1641 reflexions out of a possible 1725 for the α form and those of 978 out of 1034 for the β form were estimated visually. The unobserved reflexions were assigned intensities of half the minimum observable value. Corrections for Lorentz and polarization factors were applied in the usual way, while that for absorption was neglected.

* Presented in part at the Ninth International Congress of Crystallography, Kyoto, Japan, 1972.

Structure determination of the α and β forms

From a three-dimensional Patterson map of the α form, the positions of Cl, O and N atoms could be obtained. On the basis of the contributions of these three atoms, the coordinates of the atoms in the molecule were first refined by two-dimensional Fourier syntheses. Three-dimensional refinement was then carried out by the block-diagonal least-squares method with anisotropic thermal parameters for non-hydrogen atoms. At a later stage of refinement, the hydrogen atoms were included in the calculations with a fixed thermal parameter ($B=3.5 \text{ \AA}^2$) and fixed positional parameters deduced from the geometry of the molecule. The weighting scheme at first was $w=1-\exp(-30s^2)$ and at a later stage $w=1-\exp(-20s^2)$, where $s=\sin \theta/\lambda$ (Wa-

tanabé & Takaki, 1964). The final R index was 0.097.

A trial structure of the β form was deduced from the fact that the intensities of $hk0$ are approximately equal to those of the α form and from the consideration of the space group of the β form. Three-dimensional refinement of this model was carried out with the same procedure as that applied to the α form. The final R index was 0.065.

The atomic parameters and thermal parameters for both forms are given in Table 2.* From the considera-

* A table of observed and calculated structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30564 (13 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1. *The crystal data of the four forms of o-chlorobenzamide*

Form	Chemical formula: C_7H_6NOCl M.W. 155.6 $\mu(\text{Cu } K\alpha)=37.0 \text{ cm}^{-1}$			$D_s(\alpha \text{ form})=1.353 \text{ g cm}^{-3}$ $D_s(\beta \text{ form})=1.370 \text{ g cm}^{-3}$		Space group	Z
	a (\AA)	b (\AA)	c (\AA)	β	Absent spectra		
α	14.127 ± 0.004	10.683 ± 0.003	5.051 ± 0.003	$90.2^\circ \pm 0.03^\circ$	$h0l; h+l$ is odd $0k0; k$ is odd	$P2_1/n$	4
β	14.030 ± 0.004	10.599 ± 0.003	5.064 ± 0.002		$h00; h$ is odd $0k0; k$ is odd $00l; l$ is odd	$P2_12_12_1$	4
γ	14.037 ± 0.005	(10.64)	5.058 ± 0.005	90.0°	$h00; h$ is odd $00l; l$ is odd		4
δ	(28.07)	(10.64)	(5.06)	90.0°	$h00; h$ is $4n \pm 1$ and $4n \pm 2$ $00l; l$ is odd		8

The values of b for γ and δ are the average value of those of α and β .
The value of a of δ is taken as twice that of γ .

Table 2. *Final atomic and thermal parameters*

Anisotropic thermal parameters are of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$. All values are multiplied by 10^4 , and standard deviations in the last figures quoted, as given by the final round of least-squares analysis, are shown in parentheses.

 α Form

	x/a	y/b	z/c	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
O	-1469 (25)	546 (30)	4433 (22)	45 (1)	134 (3)	218 (8)	-41 (3)	28 (5)	2 (8)
N	-1631 (34)	573 (43)	21 (29)	53 (2)	171 (5)	226 (11)	-55 (5)	4 (7)	25 (11)
C(1)	-1140 (34)	746 (37)	2229 (30)	42 (2)	93 (4)	217 (11)	-10 (4)	5 (7)	9 (10)
C(2)	-135 (34)	1166 (39)	1872 (35)	37 (2)	91 (4)	344 (14)	-5 (4)	25 (7)	36 (11)
C(3)	255 (41)	2138 (44)	3327 (42)	51 (2)	105 (4)	455 (17)	-38 (5)	27 (9)	27 (14)
C(4)	1185 (54)	2469 (63)	3049 (68)	62 (3)	153 (6)	915 (34)	-95 (7)	20 (15)	-13 (24)
C(5)	1743 (54)	1830 (82)	1305 (81)	48 (3)	226 (10)	1132 (44)	-61 (8)	118 (17)	48 (34)
C(6)	1388 (56)	889 (71)	-186 (75)	58 (3)	183 (8)	1029 (39)	14 (8)	219 (17)	-33 (28)
C(7)	448 (46)	538 (54)	92 (47)	57 (2)	141 (5)	516 (20)	-4 (6)	115 (11)	-68 (17)
Cl	-435 (14)	3010 (13)	5497 (14)	87 (1)	102 (1)	639 (6)	-44 (2)	106 (3)	-148 (4)

 β Form

	x/a	y/b	z/c	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
O	-1477 (33)	495 (39)	4151 (28)	47 (2)	133 (4)	89 (9)	-41 (5)	20 (7)	-2 (12)
N	-1583 (41)	571 (53)	-245 (34)	52 (2)	168 (6)	57 (12)	-60 (6)	-10 (9)	-6 (15)
C(1)	-1112 (44)	716 (46)	1997 (40)	43 (2)	85 (4)	95 (13)	-12 (5)	-2 (9)	-15 (14)
C(2)	-106 (42)	1148 (47)	1762 (44)	37 (2)	84 (4)	161 (15)	-13 (5)	7 (10)	21 (14)
C(3)	274 (45)	2115 (49)	3293 (47)	44 (2)	81 (4)	274 (17)	-14 (6)	-11 (11)	5 (16)
C(4)	1202 (57)	2466 (65)	3078 (71)	50 (3)	118 (6)	545 (30)	-59 (7)	3 (17)	-31 (25)
C(5)	1802 (59)	1834 (85)	1338 (85)	45 (3)	178 (9)	767 (42)	-50 (9)	59 (19)	15 (36)
C(6)	1450 (58)	880 (68)	-194 (80)	51 (3)	146 (7)	610 (34)	11 (7)	122 (19)	-8 (29)
C(7)	509 (53)	532 (56)	18 (51)	52 (3)	118 (5)	315 (20)	-4 (7)	73 (14)	-22 (19)
Cl	-446 (15)	2969 (13)	5450 (13)	70 (1)	91 (1)	331 (5)	-23 (2)	31 (4)	-91 (4)

tion of the structural relationship between the α and β forms. the coordinates of the equivalent atomic positions are chosen as follows: x, y, z ; $\bar{x}, \frac{1}{2} + y, \bar{z}$; $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$; $\frac{1}{2} - x, \bar{y}, \frac{1}{2} - z$ for the α form and x, y, z ; $\bar{x}, \frac{1}{2} + y, \bar{z}$; $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} - z$; $\frac{1}{2} - x, \bar{y}, \frac{1}{2} + z$ for the β form.

The numerical calculations were performed on the HITAC 5020E computer of the Computer Centre of Tokyo University using the program *PAMI* written by I. Ueda for Patterson synthesis and *HBL5 IV* written by Y. Okaya and T. Ashida for the least-squares refinement.

Discussion

Molecular structures in the α and β forms

The values of the bond lengths and bond angles of the molecules in the α and β forms are shown in Fig. 1.

The mean plane through the six carbon atoms of the benzene ring and the plane through atoms C(1), N, O of the amide group are described by the following equations:

Benzene ring

$$-0.2524X + 0.6484Y - 0.7182Z' = 0.1812$$

for the α form

$$-0.2388X + 0.6572Y - 0.7148Z = 0.1947$$

for the β form

Amide group

$$-0.3274X + 0.9448Y + 0.0445Z' = 1.3269$$

for the α form

$$-0.3152X + 0.9474Y + 0.0553Z = 1.2662$$

for the β form

where X, Y, Z' and X, Y, Z are referred to the orthogonal axes a, b, c^* and a, b, c for the α and β forms respectively. The displacements of the six carbon atoms from the ring plane are not significant, and the benzene rings of both forms may be assumed to be strictly planar (see Table 3). The large deviations of the atoms N and O above and below the ring plane correspond to twist, relative to the benzene ring, of 48.5° and 48.8° of the amide group about the C(1)-C(2) bond for the α and β forms. These large angles of twist can be explained by the steric hindrance between the oxygen atom in the amide group and the chlorine atom in the *ortho* position of the ring. The significant displacements of the atoms C(1) and Cl away from one another may also contribute towards relieving the strain.

Table 3. Deviations of the atoms from the 'best' plane defined by the six carbon atoms (Å)

	α Form	β Form
O	-0.888	-0.858
N	0.786	0.822
C(1)	-0.068	-0.046
C(2)	-0.005	0.003
C(3)	0.003	-0.005
C(4)	0.003	0.006
C(5)	-0.007	-0.005
C(6)	0.007	0.002
C(7)	-0.003	-0.001
Cl	0.068	0.050

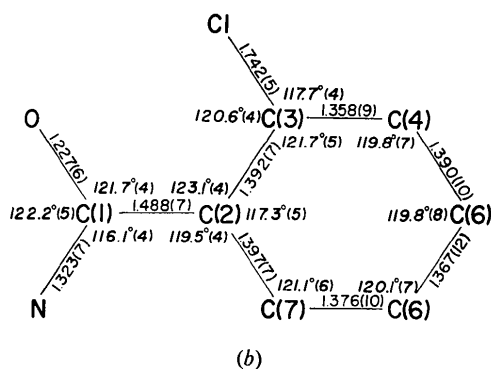
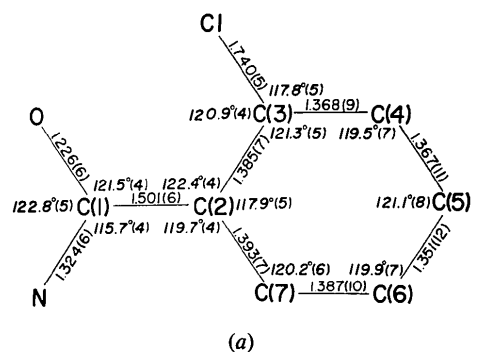


Fig. 1. Bond distances and angles with standard deviations in parentheses. (a) α Form. (b) β Form.

The mean length of the C-C bonds in the benzene ring is 1.375 Å for the α form and 1.380 Å for the β form. The intramolecular distances O-Cl and C(1)-Cl are 3.057 and 3.092 Å in the α form and 3.065 and 3.104 Å in the β form.

It is to be noted that the molecular dimensions found in the two different crystalline forms are nearly equal within the accuracy of measurement. The largest difference in the equivalent bond lengths of the molecule in the two forms is 0.023 Å [C(4)-C(5)], which corresponds to about twice the standard deviation.

Inspection of the thermal motions of the atoms derived from the anisotropic thermal parameters in Table 2, shows that in the α form the molecule makes an angular oscillation around the centre of a dimer, and in the β form the centre of the angular oscillation lies approximately on the centre of mass of the molecule. The difference between the thermal motions in the two forms is probably due to their hydrogen-bonding systems.

In order to examine the effect on the bond lengths and bond angles of changing the weighting scheme in the least-squares refinement, calculations using the scheme $w = 1$ if $F_o \leq F_{\max}$ ($= 25$), $w = F_{\max}/F_o$ if $F_o > F_{\max}$

were carried out, and the following results obtained. The largest difference between the bond lengths in the α form is 0.009 Å [C(2)–C(3) and C(5)–C(6)] which is comparable with the estimated standard deviation, and the mean C–C bond length in the benzene ring is 1.376 Å. The largest difference between the bond angles is 0.9° [C(5)C(6)C(7)]. In the β form, the largest difference between the bond lengths is 0.016 Å [C(5)–C(6)] which is a little larger than the standard deviation, and the mean C–C bond length in the benzene ring is 1.380 Å. The largest difference between the bond angles is 0.5° [C(2)C(3)C(4) and C(5)C(6)C(7)]. The *R* indices obtained for the α and β forms were 0.101 and 0.069. Though small differences in the bond lengths and bond angles were found, they are not considered to be significant.

Structures of the four polymorphs

The projections of the structures of the α and β forms along **b** are shown in Fig. 2. It can be seen that the crystals of both forms are built up by a stacking of layers along **a**; each layer consists of molecules related by 2_1 symmetry parallel to **b** and the molecular arrangement in the layer is almost the same for both forms. Within the layer, two molecules separated by a *c* translation are linked by NH...O hydrogen bonds (2.832 Å in the α form and 2.843 Å in the β form). The intermolecular distances less than 4.0 Å within the layer are listed in Table 4.

Table 4. Intermolecular distances within the layer (Å)

Symmetry code

	α Form	β Form
(I) x, y, z	(III) $\bar{x}, \frac{1}{2}+y, 1-z$	
(II) $\bar{x}, \frac{1}{2}+y, \bar{z}$	(IV) $x, y, 1+z$	
C(4) (I)–N(II)	3.71	3.63
Cl(1)–C(7) (II)	3.91	3.88
C(4) (I)–O(III)	3.55	3.52
Cl(1)–O(III)	3.82	3.81
Cl(1)–C(1) (III)	3.85	3.86
Cl(1)–C(2) (III)	3.71	3.73
Cl(1)–C(7) (III)	3.50	3.56
O(1)–N(IV)	2.832*	2.843*
O(1)–C(1) (IV)	3.97	
O(1)–C(7) (IV)	3.94	
C(3) (I)–C(6) (IV)	3.88	3.91
C(3) (I)–C(7) (IV)	3.83	3.81
C(4) (I)–C(6) (IV)	3.82	3.82
Cl(1)–N(IV)	3.86	3.71
Cl(1)–C(2) (IV)	3.80	3.76
Cl(1)–C(7) (IV)	3.73	3.72
C(1) (I)–N(IV)		3.99

* Hydrogen-bond distances

Each layer is linked to the neighbouring layers by hydrogen bonds; in the α form molecules are joined together by pairs of NH...O hydrogen bonds of length 2.951 Å across centres of symmetry to form dimers, while in the β form molecules are connected

by hydrogen bonds of length 2.963 Å to form a staggered chain along the 2_1 axis parallel to **c**. The intermolecular distances between the layers are listed in Table 5. It is very interesting that two quite different arrangements of hydrogen bonds of almost equal lengths occur stably without changing the unit-cell dimensions.

The structures of the two forms can also be described as follows. In the α form the first layer A_1 (see Fig. 2) is related to the second layer A_2 by centres of symmetry, and in the β form A_1 is related to B_2 by 2_1

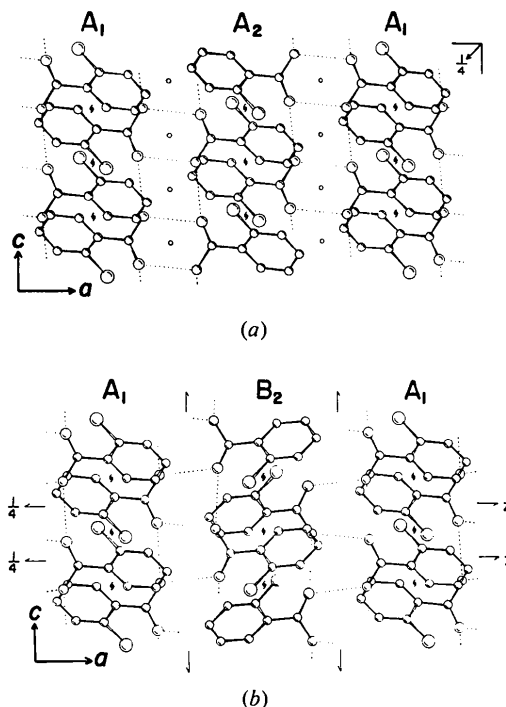


Fig. 2. Projection of the structure parallel to **b**. (a) α Form. (b) β Form. The hydrogen-bonding scheme and the molecular packing are shown.

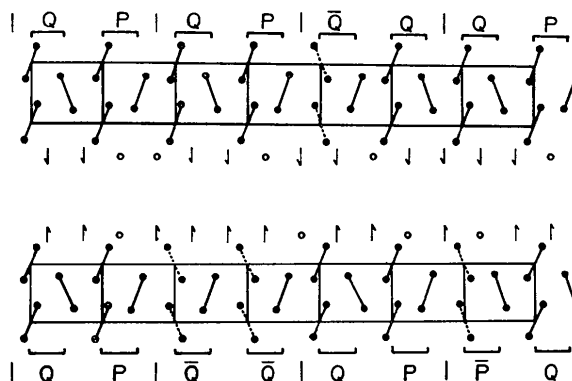


Fig. 3. A schematic drawing of the structure of the δ form projected along **b** showing the arrangement of the layers of molecules.

Table 5. Intermolecular distances between the layers (Å)

α Form			
(I)	x, y, z	(III)	$\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z$
(II)	$-\frac{1}{2}-x, \bar{y}, \frac{1}{2}-z$	(IV)	$\frac{1}{2}+x, \frac{1}{2}-y, -\frac{1}{2}+z$
	O(I)—N(II)		2.951*
	O(I)—C(1) (II)		3.75
	O(1)—O(II)		3.70
	N(I)—N(II)		3.71
	N(I)—C(1) (II)		3.72
	C(4) (I)—N(III)		3.86
	C(5) (I)—O(IV)		3.89
β Form			
(I)	x, y, z	(II)	$-\frac{1}{2}-x, \bar{y}, \frac{1}{2}+z$
(III)	$\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}-z$		
	O(I)—N(II)		2.963*
	C(4) (I)—N(III)		3.90
	C(5) (I)—O(III)		3.73
	C(5) (I)—Cl(III)		3.97

* Hydrogen-bond distances

parallel to **c**. Thus, the repeating units along **a** are A_1A_2 and A_1B_2 for the α and β forms respectively.

The same type of polymorphism has been found in the crystals of chloroacetamide (Dejace, 1955; Penfold & Simpson, 1956; Katayama, 1956). The crystal structures of three polymorphs are also of the layer type. The scheme of hydrogen bonds connecting the layers is the same as that in *o*-chlorobenzamide.

D,L-Homocysteine thiolactone hydrochloride has also been reported as having two polymorphic forms (Freer & Kraut, 1965). The molecules related by 2_1 symmetry parallel to **c** form a double-layer unit parallel to the (100) plane. The structure of HTL ($Pbc2_1$) is described in terms of a stacking of double-layer units. The symmetry element relating the double-layer units is 2_1 parallel to **c**. On the other hand, the structure of HTL ($Pbca$) consists of pairs of these double-layer units; in each pair two double-layer units are related by a centre of symmetry, and therefore the length of **a** is twice that of HTL ($Pbc2_1$).

Finally, one important remark should be made. In all the above cases of polymorphism, one layer-unit is transferred to the next by two kinds of symmetry operations yielding two different modes of stacking, while the shape of the crystal lattice remains unchanged.

Generally, in such a situation, there is a possibility that some type of structural disorder may occur. In fact, two types of disordered structures, γ and δ forms, have been found in *o*-chlorobenzamide. Both forms show one-dimensional disorder along **a** as revealed by strong diffuse streaks. On the basis of the above consideration, their structures have been determined from the intensities of Bragg reflexions and the intensity distribution of diffuse streaks. The structure of the γ form can be designated by the random stacking of P (repeat unit in the α form) and Q (repeat unit in the β form), and that of the δ form can be described as the predominant sequence of the bipartite units, QP 's. The existence of disorder in the δ form is due to the random interleaving of other units, $QQ, \bar{Q}\bar{Q}, \bar{Q}\bar{Q}, PQ, Q\bar{P}$ etc., \bar{P} and \bar{Q} being the mirror images of P and Q across the (001) plane. A schematic representation of this structure is shown in Fig. 3. A detailed account of the structure analyses of both forms will be published shortly (Takaki, Kato & Sakurai, 1974).

References

- DEJACE, J. (1955). *Acta Cryst.* **8**, 851–852.
 FREER, S. T. & KRAUT, J. (1965). *Acta Cryst.* **19**, 992–1002.
 HARADA, Y., TANIGUCHI, T., TAKAKI, Y. & SAKURAI, K. (1967). *Mem. Osaka Kyoiku Univ.* **16**, 37–43.
 HARADA, Y., TANIGUCHI, T., TAKAKI, Y. & SAKURAI, K. (1969). *Mem. Osaka Kyoiku Univ.* **18**, 1–11.
 IZUMI, T. & OKAMOTO, N. (1972). *Mem. Chubu Inst. Technol.* **8**, 139–142.
 KATAYAMA, M. (1956). *Acta Cryst.* **9**, 986–991.
 KATO, Y., TANIGUCHI, T., TAKAKI, Y. & SAKATA, K. (1967). *Mem. Osaka Kyoiku Univ.* **16**, 45–49.
 NAKATA, K., KATO, Y., TAKAKI, Y. & SAKURAI, K. (1971). *Mem. Osaka Kyoiku Univ.* **20**, 93–99.
 PENFOLD, B. R. & SIMPSON, W. S. (1956). *Acta Cryst.* **9**, 831.
 TAKAKI, Y., KATO, Y. & SAKURAI, K. (1974). To be published.
 TAKAKI, Y., TANIGUCHI, T. & SAKURAI, K. (1965). *Mem. Osaka Gakugei Univ.* **B14**, 48–55.
 TANIGUCHI, T., KATO, Y., TAKAKI, Y. & SAKATA, K. (1965). *Mem. Osaka Gakugei Univ.* **B14**, 56–64.
 WATANABÉ, T. & TAKAKI, Y. (1964). *Jap. J. Appl. Phys.* **3**, 783–788.