

scanning calorimetry measurements on  $[\text{Cu}(\text{PhCOO})_2(\text{quinoline})_2]$ .

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## Structural Analysis of the Fourfold Phase of Betaine Calcium Chloride Dihydrate at 90 K

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### Abstract

The structure of the fourfold modulated phase of betaine calcium chloride dihydrate has been determined at 90 K. The refinement was performed using two different approaches: a standard one in space group  $P2_1ca$  and a four-dimensional approach using a  $P(Pnma):(1,s,-1)$  superspace group ( $q = 0.25c^*$ ) assuming sinusoidal modulation; both refinements lead to similar  $R$  values but the four-dimensional method is more efficient for the refinement with fewer refinement parameters. The structural distortion is very similar to that of the incommensurate phase at 130 K. The amplitudes of the atomic modulations increase with respect to the incommensurate structure while the phases have approximately the same values. A symmetry-mode decomposition of the structural distortion of the

fourfold phase, as determined by the standard commensurate approach, shows that the  $A_3$  mode, corresponding to the order parameter, is predominant, in accordance with the superspace refinement with a single harmonic. Other modes also have significant amplitudes. Data at 90 K:  $(\text{CH}_3)_3\text{NCH}_2\text{-COOCaCl}_2 \cdot 2\text{H}_2\text{O}$ ,  $M_r = 264.0$ ,  $P2_1ca$ ,  $a = 10.894$  (2),  $b = 10.013$  (1),  $c = 43.237$  (6) Å,  $V = 4716$  (1) Å<sup>3</sup>,  $Z = 16$ ,  $D_x = 1.49$  g cm<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.7107$  Å,  $\mu = 9.5$  cm<sup>-1</sup>,  $F(000) = 2208$ ; for a total of 4493 independent reflections [ $I > 3\sigma(I)$ ], final  $R = 0.034$  in the commensurate refinement, and 0.046, 0.035, 0.075 and 0.56 for all, main, first- and second-order reflections, respectively, in the incommensurate refinement.

### 1. Introduction

Betaine calcium chloride dihydrate (BCCD) exhibits a long sequence of phase transitions giving rise to many commensurate and incommensurate (INC) phases modulated along the  $c$  axis with respect to a

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basic commensurate structure of *Pnma* symmetry. The behaviour of the modulation wavevector ( $\mathbf{q} = \delta\mathbf{c}^*$ ) with temperature was first reported by Brill & Eshes (1985). They found that between 164 and 127 K the modulation wavevector is incommensurate with  $\delta(T)$  varying from 0.32 to 0.285. Between 127 and 125 K a commensurate phase is found with  $\delta = \frac{2}{7}$ . Then a second INC phase ( $0.285 < \delta < 0.25$ ) appears which extends down to 116 K. Below this temperature, a sequence of commensurate phases occur with  $\delta = \frac{1}{4}$  ( $116 > T > 75$ ),  $\delta = \frac{1}{5}$  ( $75 > T > 51$ ),  $\delta = \frac{1}{6}$  ( $51 > T > 47$ ),  $\delta = 0$  ( $T < 47$  K). In general, a commensurate phase with  $\delta = n/m$  can be termed an  $m$ -fold phase, that is, its unit cell along the  $c$  axis will be  $m$  times larger than the *Pnma* basic cell. A second phase with  $\delta = \frac{1}{8}$  reported at lower temperatures was not confirmed by subsequent experiments. Between the phases just mentioned, many other high-order commensurate phases had been discovered using dielectric and pyroelectric measurements (Ribeiro, Chaves, Almeida, Albers, Kloppepiper & Müser, 1989*a,b*; Unruh, Hero & Dvorak, 1989), confirming the existence of more than 15 different phases in the temperature range from 164 down to 40 K. More recent results of elastic neutron scattering on partially deuterated BCCD confirm the existence of the  $\delta = \frac{2}{3}$  commensurate phase between the  $\delta = \frac{1}{4}$  and  $\delta = \frac{1}{5}$  phases and the non-modulated character of the phase below 47 K. Also, they point to the existence of a new INC phase between the  $\delta = \frac{2}{3}$  and  $\delta = \frac{1}{5}$  phases (Almedia, Chaves, Kiat, Schneck, Schwarz, Toledano, Ribeiro, Kloppepiper, Müser & Albers, 1991).

In terms of Landau theory, the structure of all phases appearing through the sequence of transitions can be considered as small distortions of the parent phase (room-temperature phase), with orthorhombic symmetry and space group *Pnma* (Brill, Schildkamp & Spilker, 1985). Phenomenological theory assumes a single soft-mode (order parameter) in the mechanism of the transitions and the different commensurate phases correspond to the successive lock-in of the order-parameter wavevector into commensurate values, while the modulation polarization vector is kept essentially unchanged. Under this assumption and using the extinction conditions observed in the diffraction diagram of the INC structure, the superspace group  $P(Pnma):(1,s,-1)$  was assigned to the first INC phase and the possible space groups for the commensurate phases could then be predicted (Pérez-Mato, 1988). In a previous study (Zúñiga, Ezpeleta, Pérez-Mato, Paciorek & Madariaga, 1991), the structure of the INC phase at 130 K was successfully refined using the above mentioned superspace group.

The phase studied in this paper is the one with  $\delta = \frac{1}{4}$  (hereafter labelled the fourfold phase) which

extends from 116 down to 75 K. Describing the structure of this phase as a modulation of the parent room-temperature phase, the modulation wavevector is exactly  $0.25\mathbf{c}^*$ . In the standard description, the lattice parameter  $c$  is  $4c_0$  ( $c_0$  is the value in the parent phase). According to the predictions in Pérez-Mato (1988) and the observed polar character of the phase along the  $a$  axis (Rother, Albers & Kloppepiper, 1984; Kloppepiper, Rother, Albers & Müser, 1985), the expected space group is  $P2_1ca$ . In this paper, the structure of the fourfold phase is reported and its distortion is analyzed in terms of symmetry modes and compared with that of the INC phase.

## 2. Experimental

Colourless crystals of BCCD were obtained from an aqueous solution of betaine monohydrate and calcium chloride dihydrate. A prismatic crystal of dimensions  $0.31 \times 0.15 \times 0.15$  mm was used for X-ray measurements with a CAD-4 diffractometer equipped with an open gas-flow cryostat (Cosier & Glazer, 1986). The temperature stability was within  $\pm 0.2$  K during the time of measurement.

Crystals of BCCD exhibit a remarkable temperature-dependent memory effect. Depending on the cooling rate from room temperature to the fourfold-phase temperature range, portions of the sample may remain in the incommensurate phase coexisting with the fourfold phase; this memory effect depends strongly on the time of the annealing process. The coexistence of phases can be detected by scanning the satellite reflections along the wavevector direction. In order to avoid memory effects when decreasing the temperature of the sample or due to previous thermal treatments, a virgin crystal was introduced under the  $\text{N}_2$  gas stream at 90 K. At this temperature, several superstructure reflections were scanned along the  $\mathbf{c}^*$  direction to check that their profiles corresponded to single peaks.

The lattice constants given in the *Abstract* were calculated from the setting angles of 25 accurately centered reflections ( $10 < \theta < 21^\circ$ ), used in a symmetry constrained refinement. The diffraction pattern shows two types of reflections: main reflections ( $hkl$ ,  $l = 4n$ ) associated with the reciprocal lattice of the parent phase and superstructure or satellite reflections ( $hkl$ ,  $l = 4n + 1$ ,  $4n + 2$  and  $4n + 3$ ). Intensities of main reflections out to  $(\sin\theta/\lambda)_{\max} = 0.9034 \text{ \AA}^{-1}$  with indices in the range  $0 \rightarrow 19$ ,  $0 \rightarrow 18$  and  $0 \rightarrow 76$  for  $h$ ,  $k$  and  $l$ , respectively, were measured by a  $\theta$ - $2\theta$  scan technique with intensity-dependent scan speeds varying between 4.12 and  $0.4^\circ \text{ min}^{-1}$ . Intensities of superstructure reflections out to  $(\sin\theta/\lambda)_{\max} = 0.704 \text{ \AA}^{-1}$  were measured under the same conditions as before. Four check (two main and two superstructure) reflections were measured every hour. At the

Table 1. *Positional and equivalent thermal parameters at 90 K*

$U_{eq} = \frac{1}{3}\sum U_{ii}$  for Ca, Cl, N and O atoms. The e.s.d.'s are given in parentheses.

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{eq}$ (or $U$ ) ( $\text{\AA}^2$ )
Ca1	0.19165 (6)	0.26010 (6)	-0.00642 (2)	0.0083
N1	0.4905 (2)	0.2355 (3)	0.10517 (8)	0.0145
O11	0.5336 (2)	0.2425 (2)	0.04047 (7)	0.0120
O21	0.3355 (2)	0.2776 (3)	0.03123 (7)	0.0167
Cl1	0.30292 (9)	0.45040 (8)	-0.04266 (2)	0.0157
Cl4	0.29979 (8)	0.05609 (9)	-0.03846 (2)	0.0159
O31	0.0857 (2)	0.4251 (3)	0.02325 (7)	0.0251
O34	0.0870 (2)	0.1083 (3)	0.02672 (6)	0.0186
Ca3	0.19179 (7)	0.24065 (6)	0.24386 (2)	0.0107
N3	0.4890 (2)	0.2202 (2)	0.35483 (7)	0.0128
O13	0.5340 (2)	0.2385 (2)	0.29068 (7)	0.0139
O23	0.3394 (2)	0.2619 (3)	0.27945 (8)	0.0257
Cl5	0.29132 (8)	0.44788 (9)	0.20968 (2)	0.0138
Cl8	0.31461 (7)	0.05426 (9)	0.20898 (2)	0.0131
O35	0.0763 (2)	0.3796 (3)	0.27703 (6)	0.0147
O38	0.0988 (2)	0.0650 (3)	0.27247 (7)	0.0200
Ca2	0.30542 (7)	0.74901 (7)	0.11881 (2)	0.0120
N2	0.0103 (2)	0.7228 (3)	0.23102 (8)	0.0128
O12	0.9650 (2)	0.7442 (3)	0.16507 (8)	0.0186
O22	0.1625 (2)	0.7740 (3)	0.15532 (9)	0.0214
Cl2	0.18472 (9)	0.55790 (9)	0.08534 (2)	0.0173
Cl3	0.20106 (8)	0.95091 (8)	0.08354 (2)	0.0128
O32	0.4022 (2)	0.5809 (3)	0.14886 (7)	0.0196
O33	0.4168 (2)	0.8959 (3)	0.15079 (7)	0.0181
Ca4	0.80475 (6)	0.73732 (6)	0.13146 (2)	0.0081
N4	0.5107 (2)	0.7304 (3)	0.01950 (8)	0.0169
O14	0.4615 (2)	0.7420 (3)	0.08440 (8)	0.0190
O24	0.6668 (2)	0.7573 (3)	0.09379 (8)	0.0226
Cl6	0.70484 (8)	0.94709 (9)	0.16454 (2)	0.0154
Cl7	0.68426 (8)	0.55186 (9)	0.16622 (2)	0.0167
O36	0.9177 (2)	0.8808 (3)	0.09770 (7)	0.0216
O37	0.9016 (2)	0.5651 (3)	0.10185 (6)	0.0123
Cl1	0.4284 (2)	0.2359 (3)	0.1369 (1)	0.0129
C31	0.3910 (2)	0.2550 (3)	0.08293 (8)	0.0085
C41	0.4232 (2)	0.2587 (3)	0.04828 (7)	0.0022
C21	0.5764 (2)	0.3541 (4)	0.10410 (8)	0.0135
C24	0.5523 (2)	0.1036 (4)	0.10014 (9)	0.0140
Cl3	0.4406 (2)	0.2236 (4)	0.38751 (9)	0.0131
C33	0.3891 (2)	0.2590 (3)	0.33273 (9)	0.0121
C43	0.4262 (2)	0.2536 (3)	0.2979 (1)	0.0162
C25	0.5840 (2)	0.3304 (4)	0.3550 (1)	0.0190
C28	0.5574 (2)	0.1001 (4)	0.35054 (9)	0.0160
C12	0.0729 (2)	0.7091 (4)	0.26170 (9)	0.0143
C32	0.1127 (2)	0.7496 (3)	0.20629 (9)	0.0118
C42	0.0714 (2)	0.7539 (3)	0.17258 (9)	0.0104
C22	0.9611 (2)	0.5790 (4)	0.22245 (8)	0.0109
C23	0.9078 (2)	0.8209 (4)	0.23135 (8)	0.0125
C14	0.5789 (2)	0.7218 (5)	-0.0112 (1)	0.0320
C34	0.6106 (2)	0.7385 (3)	0.04253 (9)	0.0095
C44	0.5757 (2)	0.7441 (3)	0.0757 (1)	0.0185
C26	0.4256 (2)	0.8522 (5)	0.0204 (1)	0.0256
C27	0.4505 (2)	0.5874 (5)	0.0261 (1)	0.0299

10 102 collected reflections (4274 main, 5828 superstructure), 9140 independent reflections were obtained (3921, 5219), of which 4493 (2673, 1820) had observed intensities according to the criterion  $I > 3\sigma(I)$ .

### 3. Structure refinement

#### 3.1. Commensurate refinement

For reduction of the data to  $|F|$  moduli and refinement of the structure in the commensurate model, the *XRAY72* system of programs (Stewart, Kruger, Ammon, Dickinson & Hall, 1972) was used. Atomic scattering factors of neutral Ca, Cl, O, N and C (Cromer & Mann, 1968), H (Stewart, Davidson & Simpson, 1965), and anomalous-dispersion terms for Ca and Cl (Cromer & Liberman, 1970) were used for the structure-factor calculations. The structure was solved by a least-squares method using as starting parameters the atomic coordinates of the incommensurate structure (Zúñiga *et al.*, 1991) calculated for four consecutive cells and with the global phase of the INC modulation equal to  $\pi/8$ . This value of the global phase is the appropriate value to obtain the  $P2_1ca$  space group from the  $P(Pnma):(1,s,-1)$  superspace group (Pérez-Mato, 1988). The function minimized was  $\sum w(\Delta F)^2$  with  $w = 1/\sigma^2(F)$ . The H atoms were included in the last steps of the refinement with soft-restricted C—H and O—H distances to 1.09 and 0.95 Å, and H—C—H and H—O—H angles to 109.5 and 104.5°. Atoms of Ca, Cl, N and O were refined with anisotropic thermal displacements whereas C and H atoms were refined with isotropic ones. In the last step of the refinement, a total of 549 parameters were varied; the maximum final parameter shift/e.s.d. was 1.1. The residual based on  $F$  values is  $wR = 0.046$  with a goodness of fit of 1.71. The atomic parameters are reported in Table 1.\*

#### 3.2. Four-dimensional refinement

The structure has also been refined as an incommensurately modulated structure, disregarding the fact that the actual modulation wavevector is in fact commensurate. In a one-dimensional displacive modulated structure, the atomic position  $\mathbf{r}(\mathbf{l}, \mu)$  of atom  $\mu$  in cell  $\mathbf{l}$  can be expressed in the form:

$$\mathbf{r}(\mathbf{l}, \mu) = \mathbf{l} + \mathbf{r}_o^\mu + \frac{1}{2} \sum_n \mathbf{u}_n^\mu \exp[2\pi i n \mathbf{q} \cdot (\mathbf{l} + \mathbf{r}_o^\mu)] \quad (1)$$

where  $\mathbf{r}_o^\mu$  is the average position in the basic cell and

\* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54729 (34 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AL0497]

end of the measurement (which extended over 160 h), the main check reflections showed a linear intensity decay of 4.5% whereas for the superstructure check reflections this value was 37%. Despite the strong intensity decay observed for the superstructure reflections, there was no observable broadening in their profiles. According to the different behaviour of the standard main and superstructure reflections, a different intensity-decay correction was applied for each group of reflections. The backgrounds were evaluated by analyzing scan profiles (Schwarzenbach, 1977). The standard deviations of intensities were obtained from counting statistics. Lorentz-polarization corrections were applied but no absorption correction was performed. From a total of

$u_n^\mu$  are complex Fourier vectorial amplitudes with  $u_n^\mu = u_{-n}^{\mu*}$ . In our case, the basic cell corresponds to the subcell  $c_0 = c/4$  of the actual fourfold commensurate cell. For atoms  $\mu$  and  $\nu$  related by a superspace symmetry operation  $\{R|\mathbf{t},\tau\}$  of the superspace group, the complex amplitudes satisfy the relation:

$$u_n^\nu = Ru_{\Gamma(R)n}^\mu \exp(-2\pi i n \tau_o) \quad (2)$$

where  $\Gamma(R) = +1(-1)$  if  $R\mathbf{q} = +\mathbf{q}(-\mathbf{q})$  and  $\tau_o = \tau + \mathbf{q} \cdot \mathbf{t}$  (Pérez-Mato, Madariaga, Zúñiga & Garcia-Arribas, 1987). In the case of atoms placed on special positions, the application of (2) with  $\mu = \nu$  yields restrictions on the Fourier amplitudes. In our case the wavevector is  $\mathbf{q} = 0.25\mathbf{c}^*$  and the superspace group is  $P(Pnma):(1,s,-1)$ . The choice of this superspace group follows automatically if we consider this phase as resulting from the INC structure determined in Zúñiga *et al.* (1991) when the modulation wavevector locks into the rational value  $\frac{1}{4}$ . The  $Pnma$  average structure ( $Z = 4$ ) has 18 atoms in the asymmetric unit, eight of them in the mirror plane (Brill, Schildkamp & Spilker, 1985). These positions remain special in the modulated structure with respect to the superspace symmetry element  $\{\sigma_y, |0, \frac{1}{2}, 0, \frac{1}{2}\}$ . The application of this operation in (2) gives the following restrictions for the amplitudes of the modulation of such atoms:

$$\begin{aligned} (u_y)_n &= 0 & \text{if } n = \text{even,} \\ (u_x)_n &= (u_z)_n = 0 & \text{if } n = \text{odd.} \end{aligned}$$

The refinement of the structure was performed with a modified version of the *MSR* (modulated structure refinement) program (Paciorek & Uszynski, 1987). In this new version it is possible to refine the complex Fourier amplitudes in the forms (a) moduli and phases or (b) real and imaginary parts:

$$(a) \quad u(t) = \sum_{n > 0} A_n \cos[2\pi(nt + \varphi_n)]$$

$$(b) \quad u(t) = \sum_{n > 0} [a_n \cos(2\pi nt) + b_n \sin(2\pi nt)]$$

where  $u(t)$  is the modulation function corresponding to any structural parameter and  $t$  is the so-called internal coordinate which varies continuously from 0 to 1 corresponding to the set of values of  $\mathbf{q} \cdot (\mathbf{l} + \mathbf{r}^\mu)$  (mod. 1) in equation (1). Note that in the above equations the zero-order harmonics are not refined explicitly, being included within the refined atomic parameters of the average structure. Choice between forms (a) or (b) not only gives an alternative description for the modulation functions but also offers different possibilities in the refinement process (Pérez-Mato, Madariaga & Zúñiga, 1989). In our refinement alternative (a) was chosen.

In this four-dimensional description, the diffraction pattern is interpreted with respect to the

reciprocal-lattice basis of the parent phase and all the reflections are indexed with four indices

$$\mathbf{H} = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^* + m\mathbf{q}.$$

The main reflections are those with  $m = 0$  and correspond to those superstructure reflections with index  $l = 4n$  in the commensurate description whereas satellite reflections with  $m = +1, -1$  and  $+2$  correspond to the superstructure reflections with  $l = 4n + 1, 4n + 3$  and  $4n + 2$ , respectively. According to this scheme, the distribution of the independent data set leads to 4274 main, 3358 (1778 observed) first-order satellite and 1861 (43 observed) second-order satellite reflections, respectively. The resulting extinction rules for the superspace group are generally satisfied by the measured intensities. The intensities were reduced to  $|F|$  moduli as described in §3.1.

Using the superspace model for the structure including the corresponding structure-factor expression is equivalent to neglecting the superposition of high-order satellites with lower-order ones; that is, in principle, third-order satellites ( $h, k, l, 3$ ) superpose with first-order satellites ( $h, k, l + 1, -1$ ), second-order satellites ( $h, k, l, 2$ ) superpose with ( $h, k, l + 1, -2$ ) and so on. In our case, as even the second-order satellite reflections are very weak (43 observed from 1861 measured), this superposition effect can be assumed to be negligible. Moreover, we considered a sinusoidal modulation [only one harmonic in (1)].

Using as starting parameters those of the incommensurate structure at 130 K, the refinement converges in a few cycles. All non-H atoms were refined with non-modulated anisotropic thermal parameters. In the last steps of the refinement, the H atoms were included in the calculation of the structure factors and their modulation functions refined with isotropic temperature factors. As the refinement of the H-atom modulations was unstable, the bond lengths O—H and C—H were restricted so that the variation of these distances throughout the crystal is maintained to within  $\pm 0.025 \text{ \AA}$  of the prescribed value; the H—O—H angle was also restricted to  $104.5^\circ$  (to within  $\pm 1.8^\circ$ ). The final atomic parameters including average coordinates, amplitudes and phases of atomic modulations and equivalent isotropic thermal displacements are given in Tables 2(a) and 2(b).<sup>\*</sup> The final calculated  $R$  ( $wR$ ) values based on 4493 observations and 169 variables are 0.046 (0.082), 0.035 (0.059), 0.075 (0.115) and 0.56 (0.72) for all, main, first-order satellite and second-order satellite reflections, respectively, with a goodness of fit of 3.60. These values can be compared with the corresponding values calculated for main reflections ( $R = 0.028$ ), superstructure reflections with  $l = 4n + 1, 4n + 3$  ( $R$

<sup>\*</sup> Anisotropic thermal parameters and atomic parameters for H atoms have been deposited: see deposition footnote.

Table 2. *Final atomic parameters at 90 K*

## (a) Average structure

The atomic coordinates refer to the basic cell ( $c_o = c/4$ ).  $U_{eq} = \frac{1}{3}\sum_i U_{ii}$ . Standard deviations are given in parentheses.

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{eq}$ (or $U$ ) ( $\text{\AA}^2$ )
Ca	0.19342 (4)	0.2500	0.22480 (4)	0.0097 (2)
Cl	0.30413 (4)	0.44709 (4)	0.08782 (4)	0.0151 (3)
C1	0.4311 (3)	0.2500	0.7972 (3)	0.0208 (8)
C2	0.5665 (2)	0.3713 (3)	0.6590 (2)	0.0179 (7)
C3	0.3893 (3)	0.2500	0.5793 (2)	0.0126 (4)
C4	0.4257 (2)	0.2500	0.4427 (2)	0.0118 (4)
N	0.4898 (2)	0.2500	0.6716 (2)	0.0075 (4)
O1	0.5349 (2)	0.2500	0.4115 (2)	0.0158 (4)
O2	0.3359 (2)	0.2500	0.3725 (2)	0.0231 (7)
O3	0.0887 (1)	0.4081 (2)	0.3499 (1)	0.0168 (4)

(b) Amplitudes ( $\times 10^5$ ) in units of fractional coordinates and phases ( $\times 10^3$ ) of the modulation functions

Modulating functions are:  $u_i(t) = a_i \cos[2\pi(t + \varphi_i)]$ ,  $i = x, y, z$ . Standard deviations are given in parentheses.

	$a_x$	$\varphi_x$	$a_y$	$\varphi_y$	$a_z$	$\varphi_z$
Ca	0	0	1373 (6)	132 (1)	0	0
Cl	1302 (5)	271 (1)	-401 (6)	460 (2)	-687 (6)	55 (1)
C1	0	0	4109 (46)	173 (2)	0	0
C2	-2447 (28)	231 (3)	5016 (32)	213 (1)	-1686 (28)	221 (3)
C3	0	0	628 (35)	-72 (9)	0	0
C4	0	0	848 (34)	-71 (7)	0	0
N	0	0	3604 (29)	198 (2)	0	0
O1	0	0	1129 (25)	265 (4)	0	0
O2	0	0	2788 (31)	-145 (2)	0	0
O3	1126 (18)	224 (3)	3205 (20)	154 (1)	-1080 (18)	146 (3)

= 0.092), and superstructure reflections with  $l = 4n + 2$  ( $R = 0.33$ ) in the commensurate refinement.

A parallel refinement, including a second harmonic in the atomic modulation functions for all non-H atoms, was also performed. This refinement leads to similar results, showing that the amplitudes of the second harmonic are in general one order of magnitude lower than those of the first harmonic, except for atoms C3 and C4. For these two atoms the amplitudes corresponding to the first and second harmonics are comparable. In this case, the agreement factors,  $R$  ( $wR$ ), based on 4493 observations and 215 variables are 0.043 (0.079), 0.033 (0.057), 0.069 (0.112) and 0.50 (0.69) for all, main, first-order satellite and second-order satellite reflections respectively.

## 4. Symmetry-mode analysis

To compare the structures of the INC and fourfold phases in a quantitative way, the structural distortion relating the fourfold phase and the basic structure is analysed in terms of the symmetry modes of the latter. The fundamentals of the method are explained in Pérez-Mato, Gaztelua, Madariaga & Tello (1986), while examples of this type of analysis can also be found in Withers, Thompson & Hyde (1989), Withers, Wallenberg, Bevan, Thompson & Hyde (1989) and Withers, Feng & Lu (1990). This procedure provides the relative weight of the symmetry modes present in the total distortion. The super-space symmetry for the INC phase implies that each

harmonic of the atomic modulation functions describing the INC distortion correspond to a certain symmetry mode. As a result, it is possible to compare the amplitudes of the symmetry modes appearing in the distortion of the fourfold phase with the atomic modulation amplitudes of the INC phase. The first step in this type of analysis is to determine the symmetry modes contributing to the distortion of the fourfold phase. This is done taking into account the fact that these modes have to transform according to irreducible representations (and certain directions in the representation space), whose invariance group contains the space group of the distorted phase as a subgroup.

In our case, the irreducible representations of  $Pnma$  compatible with the  $P2_1ca$  symmetry of the fourfold phase are  $A_{1g}$ ,  $B_{3u}$  (at  $\mathbf{k} = 0$ ),  $A_2$ ,  $A_3$  (at  $\mathbf{k} = \frac{1}{2}c^*$ ) and  $Z_1$  (at  $\mathbf{k} = \frac{1}{2}c^*$ ).  $A_{1g}$  is the fully symmetric representation for the  $mmm$  point group;  $B_{3u}$  is the antisymmetric representation for  $C_{2y}$ ,  $C_{2z}$ ,  $I$  and  $\sigma_x$ ;  $A_2$  the antisymmetric representation for  $\sigma_x$  and  $\sigma_y$ ;  $A_3$  the antisymmetric representation for  $\sigma_x$  and  $C_{2z}$ ;  $Z_1$  corresponding to the weighted representation  $\tau_1$  [ $X(\sigma_y) = +2$ ] at the point  $\mathbf{k} = \frac{1}{2}c^*$  (Kovalev, 1965).  $A_3$  is the symmetry of the order parameter in the INC phase, and it can be considered to be the symmetry of the primary mode, while the other irreducible representations correspond to secondary modes.

In the basic structure of BCCD, seven of the ten atoms (excluding hydrogens) in the asymmetric unit lie on the mirror plane, while the remaining three atoms occupy general positions. Using standard group-theoretical methods, the total distortion for each set of symmetry-related atoms in special and general positions can be expressed by the superposition of the following symmetry modes. For the special position there are 12 symmetry-mode contributions:  $A_g(x) + A_g(z) + B_{3u}(x) + B_{3u}(z) + 2A_2(y) + 2A_3(y) + 2Z_1(x) + 2Z_1(z)$ . The displacement direction for each mode is indicated in parentheses. For general positions there are 24 contributions:  $A_g(x) + A_g(y) + A_g(z) + B_{3u}(x) + B_{3u}(y) + B_{3u}(z) + 2A_2(x) + 2A_2(y) + 2A_2(z) + 2A_3(x) + 2A_3(y) + 2A_3(z) + 2Z_1(x) + 2Z_1(y) + 2Z_1(z)$ .

Taking into account the number of atoms in each kind of position, the total number of symmetry-mode amplitudes describing the distortion is 156, in agreement with the number of free structural atomic coordinates in the fourfold phase.

Once the relevant modes had been determined, a Fourier analysis was performed to determine the weight of these modes in the total distortion. In order to relate the basic non-distorted structure to the fourfold one, an atomic displacement field  $u_\alpha(l, \mu)$  ( $\alpha = x, y, z$ ;  $\mu = 1 \dots s$ ),  $\mu$  and  $l$  being the atomic label in the unit cell and the cell label,

Table 3. Amplitudes ( $\times 10^5$ ) in units of fractional coordinates and phases ( $\times 10^3$ ) in  $2\pi$  units, of the symmetry modes in the fourfold structure

	Ca	Cl	C1	C2	C3	C4	N	O1	O2	O3
$A_4(x)$	-366	-74	622	528	82	-506	562	-424	-1062	-442
$A_4(y)$		224		430						552
$A_4(z)$	168	12	306	-538	984	794	204	84	942	-124
$B_{3u}(y)$		-8		-648						16
$B_{3u}(z)$	-18	-58	314	248	380	-142	-304	96	-170	-64
$A_2(x)$		70 548		724 -124						62 179
$A_2(y)$	94 729	84 63	1154 328	1158 347	884 393	264 508	484 199	464 179	940 -188	288 735
$A_2(z)$		190 358		616 -148						192 247
$A_3(x)$		1244 271		2326 726						1102 226
$A_3(y)$	1322 134	386 -41	3934 161	4902 206	644 -87	790 -70	3298 194	1102 253	2604 -143	3082 151
$A_3(z)$		668 555		1602 711						1020 643
$Z_1(x)$	34 -204	116 209	682 -201	366 -124	140 471	262 60	74 248	178 690	294 73	62 -34
$Z_1(y)$		58 -217		762 430						58 490
$Z_1(z)$	78 135	42 744	144 -155	132 -166	240 561	354 621	124 132	114 729	398 515	92 615

respectively, can be defined, and it can be expressed in terms of the symmetry modes already known:

$$u_\alpha(l, \mu) = \frac{1}{2} \sum_{\mathbf{q}} \sum_{\lambda} \sum_i A(\mathbf{q}, \lambda^i) \varepsilon_\alpha(\mu | \mathbf{q}, \lambda^i) \exp[i\mathbf{q} \cdot \mathbf{r}(l, \mu)] \quad (3)$$

where  $\lambda$  labels the symmetry of the mode for a given  $\mathbf{q}$  and  $i$  is an integer which numbers the modes of the same symmetry  $\lambda$  when more than one mode of that symmetry contributes to the total distortion,  $\mathbf{r}(l, \mu)$  is the position of atom  $\mu$  in the  $l$ th unit cell, and the sum over  $\mathbf{q}$  extends in this case to  $\mathbf{q} = 0, \pm \frac{1}{2}\mathbf{c}^*, \frac{1}{2}\mathbf{c}^*$ .  $\varepsilon_\alpha(\mu | \mathbf{q}, \lambda^i)$  are the symmetry modes mentioned before and  $A(\mathbf{q}, \lambda^i)$  the amplitudes of those symmetry modes, which are the magnitudes to be determined. These amplitudes are determined using the orthogonality condition satisfied by the symmetry modes  $\varepsilon_\alpha(\mu | \mathbf{q}, \lambda^i)$ . The displacement field  $u_\alpha(l, \mu)$  was determined from the comparison of the commensurate refinement of the fourfold phase reported in this paper and the room-temperature phase (Brill, Schildkamp & Spilker, 1985). The slight deformation of the Bravais lattice between the two phases was neglected.

The above mentioned displacement field (3) can be written in the following way:

$$u_\alpha(l, \mu) = \frac{1}{2} \sum_{\mathbf{q}} \sum_{\lambda} Q(\mathbf{q}, \lambda) e_\alpha(\mu | \mathbf{q}, \lambda) \exp[i\mathbf{q} \cdot \mathbf{r}(l, \mu)] \quad (4)$$

where the new magnitudes  $e_\alpha(\mu | \mathbf{q}, \lambda)$  are defined by:

$$Q(\mathbf{q}, \lambda) e_\alpha(\mu | \mathbf{q}, \lambda) = \sum_i A(\mathbf{q}, \lambda^i) \varepsilon_\alpha(\mu | \mathbf{q}, \lambda^i). \quad (5)$$

According to this definition, the sum over  $i$  will extend to one term in the case of the zone-centre modes and to two terms for the rest of the modes. The complex magnitudes  $Q(\mathbf{q}, \lambda)$  can be expressed as:

$$Q(\mathbf{q}, \lambda) = \rho(\mathbf{q}, \lambda) \exp[i\Phi(\mathbf{q}, \lambda)] \quad (6)$$

where we have chosen  $\rho(\mathbf{q}, \lambda) = 1$  for all the different modes and  $\Phi(\mathbf{q}, \lambda)$  is the restricted value of the phase of the normal coordinate  $Q(\mathbf{q}, \lambda)$ , which follows automatically when the space group of the distorted phase is imposed. In this case  $\Phi = \pi/8 + n\pi/4$  ( $n$  integer). The different possibilities given by the choice of  $n$  in this expression correspond to the

different equivalent domain choices for relating the basic and the fourfold structure. Finally, it is possible to write the magnitudes  $e_\alpha(\mu | \mathbf{q}, \lambda)$  given in (5) in terms of an amplitude and a phase; those corresponding to  $A_3$  are directly comparable with the amplitudes and phases of the atomic modulation functions of the superspace refinement. The values of these amplitudes  $|e_\alpha(\mu | \mathbf{q}, \lambda)|$  and phases  $\theta(\mu | \mathbf{q}, \lambda)$  for all non-H atoms are given in Table 3.

It should be pointed out that the amplitude of the  $B_{3u}$  mode along the  $x$  direction cannot be determined, because this mode represents a translation of all atoms along the  $x$  direction, and the origin of the fourfold structure in this direction was chosen arbitrarily due to the polar character of the space group.

## 5. Discussion

The average structure consists of (010) parallel sheets of BCCD molecules sharing O atoms of carboxyl groups. The parallel sheets are connected through  $\text{Cl} \cdots \text{H} - \text{O}$  hydrogen bonds. A projection down the  $a$  axis of the fourfold modulated structure is shown in Fig. 1.

In order to compare the atomic displacements obtained by means of the two different refinements, it is necessary to take into account for the INC model that the modulation wavevector is commensurate ( $\mathbf{q} = \frac{1}{4}\mathbf{c}^*$ ), and therefore, it can be seen from (1), that the structural distortion is repeated every four basic cells along the  $z$  axis. Thus only the values of the atomic modulation functions at four equidis-

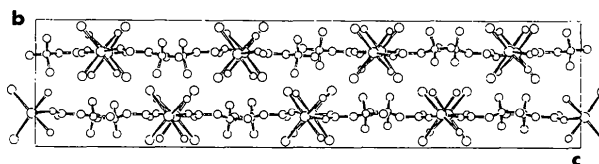
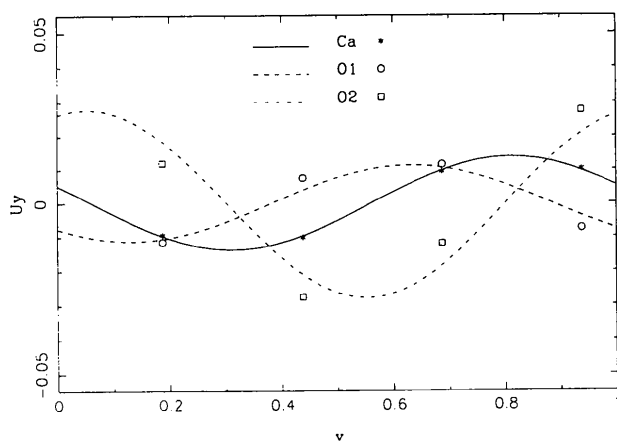
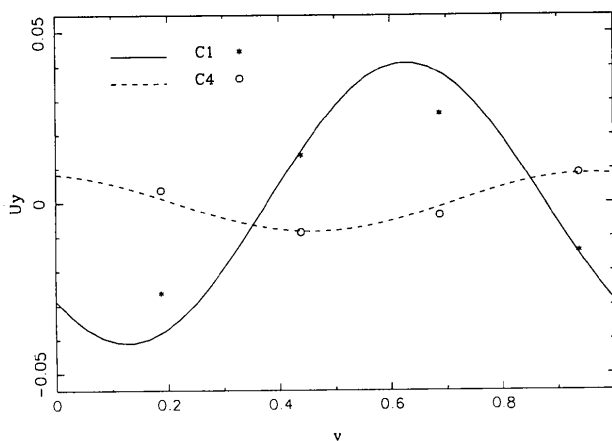


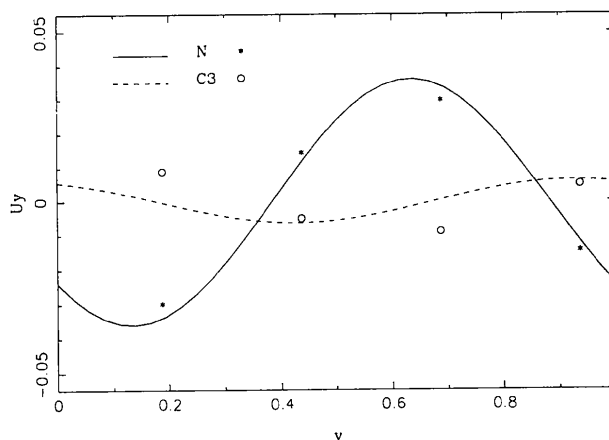
Fig. 1. Projection down the  $a$  axis of the unit cell of the fourfold structure of BCCD at 90 K



(a)



(b)



(c)

Fig. 2. Atomic modulation functions in units of fractional coordinates along the  $b$  axis of the (a) Ca, O1 and O2, (b) C1 and C4 and (c) N and C3 atoms from the superspace refinement of the structure (curves) compared with the corresponding displacements of the commensurate refinement of the fourfold phase (discrete points).

Table 4. Minimum, maximum and average interatomic distances ( $\text{\AA}$ ) along the modulation of BCCD at 90 K, with standard deviations given in parentheses

	Min.	Max.	Max. - Min.	Average
Ca-O2	2.227 (1)	2.247 (1)	0.020	2.237 (1)
Ca-O3	2.367 (2)	2.398 (2)	0.031	2.381 (2)
Ca-Cl	2.731 (1)	2.771 (1)	0.040	2.750 (1)
C4-O2	1.238 (2)	1.256 (2)	0.018	1.247 (2)
C4-O1	1.236 (2)	1.248 (2)	0.012	1.242 (2)
C4-C3	1.529 (2)	1.530 (2)	0.001	1.530 (2)
C3-N	1.481 (2)	1.530 (2)	0.049	1.506 (2)
C2-N	1.473 (4)	1.537 (3)	0.064	1.502 (4)
C1-N	1.500 (2)	1.501 (2)	0.001	1.500 (2)
C1-H1	0.94 (2)	0.99 (3)	0.05	0.96 (3)
C1-H2	0.95 (2)	0.98 (2)	0.03	0.96 (2)
C2-H3	0.92 (3)	0.98 (3)	0.06	0.95 (3)
C2-H4	0.95 (3)	1.03 (3)	0.08	0.98 (3)
C2-H5	0.94 (3)	0.97 (3)	0.03	0.95 (3)
C3-H6	0.91 (3)	0.98 (3)	0.07	0.95 (3)
O3-H7	0.91 (2)	0.98 (2)	0.07	0.94 (2)
O3-H8	0.91 (3)	0.97 (3)	0.06	0.94 (3)

tant points (distance  $\frac{1}{4}$ ) along  $v$  ( $v = \mathbf{q} \cdot \mathbf{l}$ ), corresponding to four consecutive cells, are relevant for describing the structure. In addition, the space group  $P2_1ca$  of the fourfold phase restricts the value  $v_o$ , which can be assigned to the first of the four cells, to the values  $\frac{1}{8} + n/8$  ( $n$  integer). The different values of  $v_o$  as a function of  $n$  are again connected to the different equivalent domains. With these considerations, the distortions along the  $y$  axis obtained through the two refinements are compared in Figs. 2(a-c), for all non-H atoms lying on the mirror plane in the basic structure. The atomic displacements in the four basic subcells of the fourfold structure are assigned the values 0.1875, 0.4375, 0.6875 and 0.9375 in such a way that they correspond to the subcells 1, 2, 3 and 0, respectively. They can be compared with the corresponding atomic modulation functions resulting from the superspace refinement (Table 2b), defined for all values of  $v$ . In general, these values fit well onto the continuous modulation function, with the exception of the C3 atom which has an amplitude-modulation value of 0.06  $\text{\AA}$ . In any case, the significant differences between the atomic displacements obtained from the two refinements could be attributed to the fact that the commensurate refinement includes degrees of freedom not considered in the superspace refinement (high-order harmonics). This fact is also manifest in the different goodness-of-fit and  $R$  factors obtained.

The minimum, maximum and average distances along the modulation, obtained from the four-dimensional refinement are given in Table 4. These values (and also the interatomic angles) are very similar to those of the INC structure at 130 K, indicating that the rigid-body behaviour of the BCCD molecules at 90 and 130 K is almost identical.

From Table 3, it can be seen that, in general, the  $\Lambda_3$  distortion clearly predominates in agreement with the fact that this mode corresponds to the order parameter leading to the transition sequence in

BCCD. The exceptions are atoms C3 and C4 for which the amplitudes of all symmetry modes have lower values when compared with the rest of the atoms, and the reliability of the results depends on the magnitude of these amplitudes. Now if we want to compare these results with the distortions in the INC phase at 130 K and the fourfold phase at 90 K (refined in the superspace model), it is necessary to take into account that only harmonics up to first order were refined in these cases and therefore, the symmetry of the corresponding distortions can be expressed as  $A_{1g} + A_3$ , where  $A_{1g}$  and  $A_3$  correspond to the zero and first harmonics in the atomic modulation functions, respectively. The amplitudes and phases of the  $A_3$  mode in Table 3 can therefore be compared directly with the amplitudes and phases of the first harmonic in the atomic modulation functions determined at 130 K (Table 3 of Zúñiga *et al.*, 1991) and at 90 K (Table 2(b)). Figs. 3 and 4 show these comparisons. The points in Fig. 3 have been fitted to straight lines with slopes 1.32 and 0.98 for the moduli and phases, respectively. This result shows that the primary mode maintains essentially

the same structure in the two phases, while only changing its global amplitude by a factor of 1.32. The points in Fig. 4, which were also fitted to straight lines, have slopes of 0.96 and 1.00 for the moduli and phases, respectively, indicating that the superspace refinement of the fourfold phase gives an essentially correct model for the  $A_3$  distortion, despite its radical omission of the effects of the other modes which are obviously also present in the structure, as shown above.

We can now compare the results from the symmetry-mode analysis with the phenomenological model for the transition sequence in BCCD proposed by Dvorak (1990). According to this model, two symmetry-breaking order parameters exist, so that the main structural modulation is a  $A_3 + A_2$  distortion with a single wavevector. The symmetry predicted by this model for the different phases differs in general from that resulting from the single soft-mode model (Pérez-Mato, 1988), but in the case of the fourfold phase the symmetry prediction coincides. However, the  $A_2$  contribution to the total distortion has a different origin in the two models; in

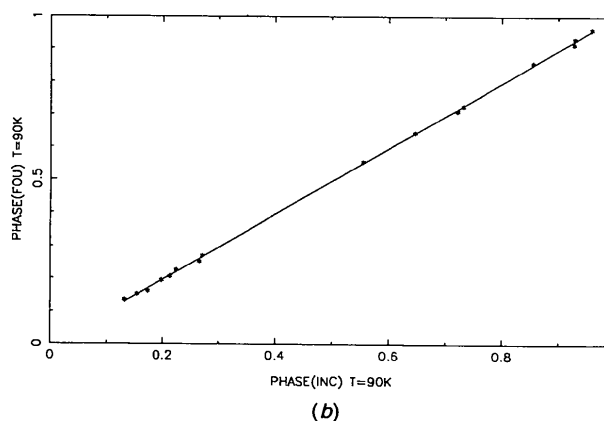
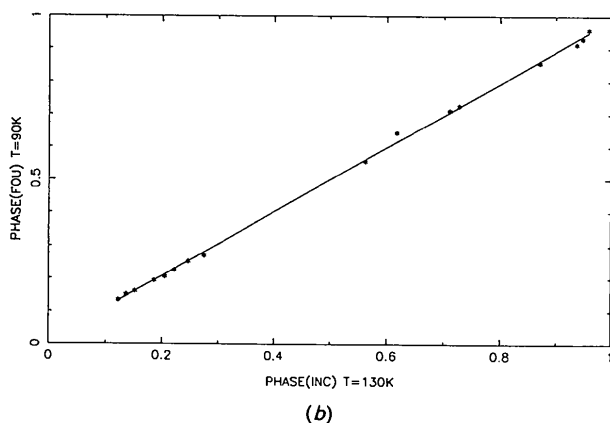
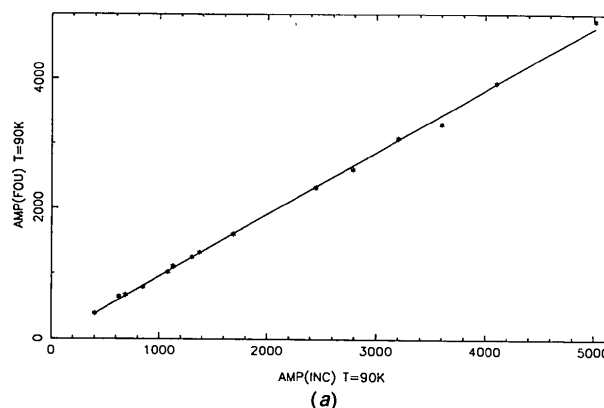
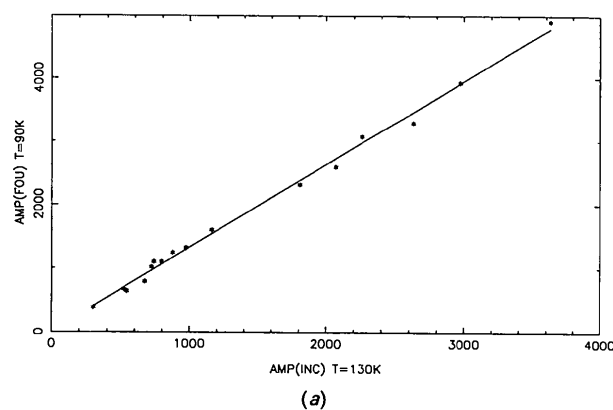


Fig. 3. Representation of (a) the moduli in relative units and (b) phases in  $2\pi$  units of the  $A_3$  mode obtained from the symmetry-mode analysis of the fourfold structure at 90 K against the corresponding ones in the INC structure at 130 K.

Fig. 4. Representation of (a) the moduli in relative units and (b) phases in  $2\pi$  units of the  $A_3$  mode obtained from the symmetry-mode analysis of the fourfold structure at 90 K against the corresponding ones in the superspace refinement at 90 K.



the single order-parameter model, the  $A_2$  distortion corresponds to a secondary mode (third harmonic of the primary mode  $A_3$ ), whereas according to the other model, it plays the role of a primary mode. Taking into account the relative weights of the  $A_3$  and  $A_2$  modes from our analysis, we think that these results support the single soft-mode model, because otherwise a larger contribution from the  $A_2$  mode could be expected. As a general conclusion to this work it can be said that the four-dimensional description and refinement of the modulated structure is comparable to the standard commensurate one. The former refinement, however, includes far fewer variables. On the other hand, we have found that the structure of the modulated fourfold phase of BCCD is essentially the same as that of the INC phase with a major contribution of the  $A_3$  mode to the distortion. Accordingly, it can be expected that the structures of the different commensurate and INC phases appearing below 75 K are similar to that of the first INC phase except for the change of wavevector values and greater amplitude of the distortion.

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## Structures of 4-Methoxy-, 5-Chloro-, 5-Nitro- and 6-Nitro-1,2-benzisothiazol-3(2H)-one 1,1-Dioxide Sodium Salt (4-Methoxy-, 5-Chloro-, 5-Nitro- and 6-Nitrosaccharin)

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#### Abstract

The crystal structures of four bitter-tasting saccharin derivatives have been solved. 4-Methoxysaccharin,

$2\text{Na}^+ \cdot 2\text{C}_8\text{H}_6\text{NO}_4\text{S}^- \cdot 3\text{CH}_3\text{OH}$ ,  $M_r = 566.5$ , monoclinic,  $P2_1/c$ ,  $a = 10.461(4)$ ,  $b = 10.942(4)$ ,  $c = 21.799(8)$  Å,  $\beta = 96.97(3)^\circ$ ,  $V = 2477(3)$  Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.519$  g cm<sup>-3</sup>,  $\lambda(\text{Cu K}\alpha) = 1.54178$  Å,  $\mu =$

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