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Polytypism in Sodium 2-Oxocaproate Crystals*

BY L. M. PANT
National Chemical Laboratory, Poona, India

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Sodium 2-oxocaproate crystals contain ordered, disordered and polytypic regions in them. The type of disorder and the structure of the polytype are described.

Crystals of sodium 2-oxocaproate,

$$CH_3(CH_2)_3COCOONa,$$

give a pattern of sharp and diffuse X-ray reflexions. It is seen from zero and higher layer Weissenberg photographs that the reflexions with $h+k+l$ even and $k+l$ even are sharp while those with $h+k+l$ even and $k+l$ odd, although sharp, appear above a background of diffuse maxima. Further, reflexions corresponding to an a axial length twice that of the normal cell appear on either side of the reflexions with $h+k+l$ even and $k+l$ odd; with respect to the double cell, these reflexions have the indices Hkl with H odd. Figs. 1 and 2 show reflexions on zero layer Weissenberg photographs taken with **c** as oscillation axis; the indices $Hk0$ shown are with respect to the double cell, *i.e.* $H=2h$. These results suggest that the crystals contain ordered, disordered and polytypic regions in them. In this communication, the type of disorder and the structure of the polytype are described.

The data already reported for the basic structure (Jain, Tavale & Biswas, 1966) are: $a=39{\cdot}46$, $b=6{\cdot}11$, $c=5{\cdot}94$ Å; space group *Iba*2. This space group has the following eight equivalent positions:

x,y,z; $x,\bar{y},\frac{1}{2}+z$; $\frac{1}{2}-x,\frac{1}{2}+y,z$; $\frac{1}{2}-x,\frac{1}{2}-y,\frac{1}{2}+z$ *A*

$\bar{x},\bar{y},z$; $\bar{x},y,\frac{1}{2}+z$; $-(\frac{1}{2}-x),\frac{1}{2}-y,z$; $-(\frac{1}{2}-x),\frac{1}{2}+y,\frac{1}{2}+z$ *B*

Each equivalent position corresponds to one molecule; the four molecules marked *A* form the repeat unit of one layer of molecules while the other four marked *B* form the repeat unit of the neighbouring layer. The disorder in the crystal consists in the appearance of any layer as displaced from its expected position in the ordered structure by $\frac{1}{2}(\mathbf{b}+\mathbf{c})$. It is clear from the equivalent points of *A* and *B* that if the *B* layer is displaced by $\frac{1}{2}(\mathbf{b}+\mathbf{c})$, the unit cell becomes *AA* instead of *AB*. For such disorder, it can be shown (Pant, 1964) that as observed, reflexions with $h+k+l$ even and $k+l$ even are sharp while those with $h+k+l$ even (*i.e.* $H/2+k+l$ even) and $k+l$ odd are diffuse; the sharp reflexions appearing above the background of diffuse maxima (*e.g.* reflexions marked 30.1.0 and 30.3.0 in Fig. 2(*a*) and (*b*) respectively) come from the ordered region in the crystal.

The structure of the polytype is, as shown later, *AABBAABB* ... The equivalent points for the unit cell of the polytype are as follows:

X,y,z;	$X,\bar{y},\frac{1}{2}+z$;	$\frac{1}{4}-X,\frac{1}{2}+y,z$;	$\frac{1}{4}-X,\frac{1}{2}-y,\frac{1}{2}+z$	*A*
$\frac{1}{4}+X,y,z$;	$\frac{1}{4}+X,\bar{y},\frac{1}{2}+z$;	$\frac{1}{2}-X,\frac{1}{2}+y,z$;	$\frac{1}{2}-X,\frac{1}{2}-y,\frac{1}{2}+z$	*A*
$\bar{X},\bar{y},z$;	$\bar{X},y,\frac{1}{2}+z$;	$-\frac{1}{4}+X,\frac{1}{2}-y,z$;	$-\frac{1}{4}+X,\frac{1}{2}+y,\frac{1}{2}+z$	*B*
$-\frac{1}{4}-X,\bar{y},z$;	$-\frac{1}{4}-X,y,\frac{1}{2}+z$;	$-\frac{1}{2}+X,\frac{1}{2}-y,z$;	$-\frac{1}{2}+X,\frac{1}{2}+y,\frac{1}{2}+z$	*B*

In the above, X corresponds to the unit cell of the polytype, therefore $x=2X$, since x corresponds to the unit cell of the basic structure. It is obvious from the equivalent points that the space group of the polytype is also *Iba*2, and the asymmetric unit consists of two molecules, one represented by (X,y,z) and the other by $(\frac{1}{4}+X,y,z)$.

From the structure factor formulae obtained with the use of the equivalent points written above, it may be shown for reflexions with $k+l$ even that as observed, reflexions from the polytype would be present for $H=4n$ only, *i.e.* for $h=2n$. These reflexions coincide with and appear with the same absolute intensity as the reflexions from the normal crystal. Similarly, it may be shown for reflexions with $k+l$ odd that only those with H odd would be present. With respect to the unit cell of the basic structure, these reflexions have the indices $h\pm\frac{1}{2},k,l$, and they appear on either side of the reflexions from the basic structure (Fig. 2). The structure factor formulae for the polytype for reflexions of the type $Hk0$ are as follows:

$$F(Hk0)=8\cos 2\pi ky\{\cos 2\pi HX-\sin 2\pi HX\}$$
for k odd and $H=4n+1$, and
$$8\cos 2\pi ky\{\cos 2\pi HX+\sin 2\pi HX\}$$
for k odd and $H=4n-1$.

For k odd and H even, $F(Hk0)=0$.

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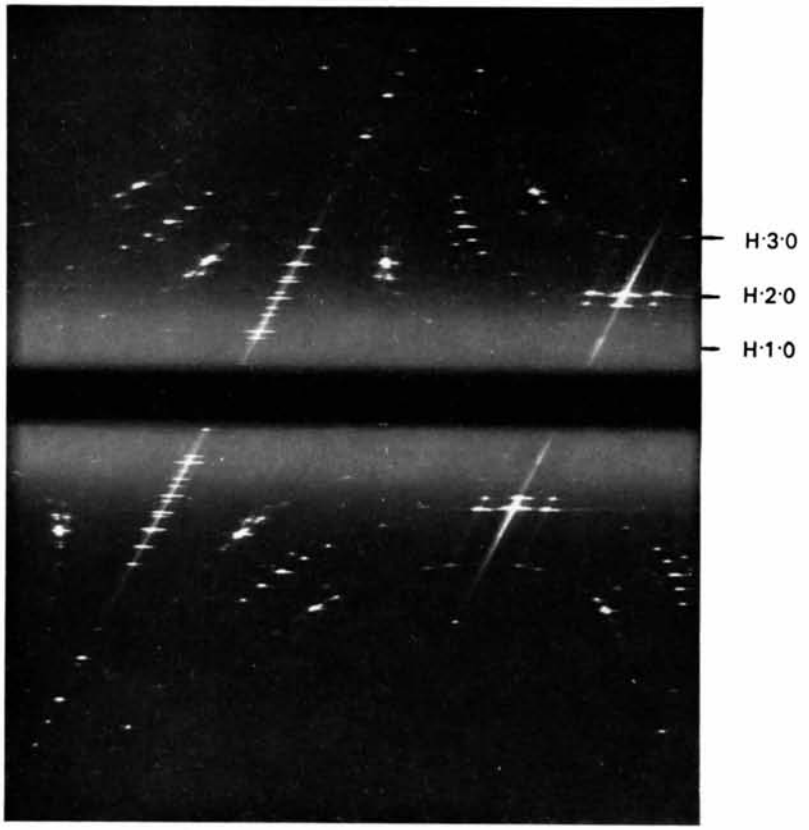

Fig. 1. Zero layer Weissenberg photograph. Oscillation axis c. Cu radiation, 30kV, 17mA, exposure 16hr.

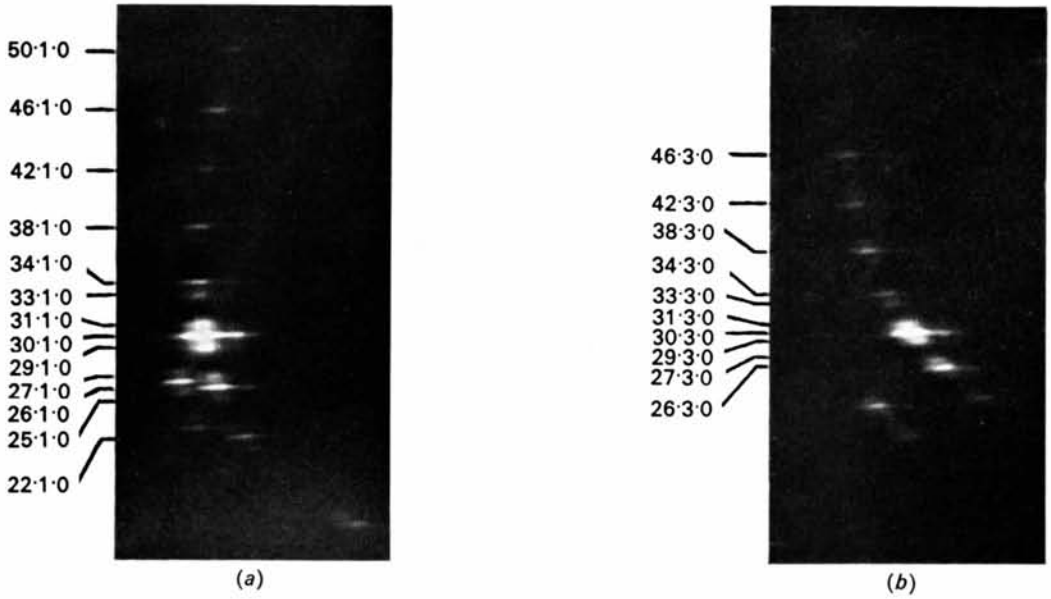

Fig. 2. Enlargements of parts of Fig. 1, showing (*a*) *H*10 reflexions, (*b*) *H*30 reflexions.

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Table 1. *Observed and calculated structure factors*

H	k	0	$\|F_o\|$	F_c	*H*	*k*	0	$\|F_o\|$	F_c
23	1	0	28	$\overline{38}$	23	3	0	23	38
25	1	0	47	49	25	3	0	42	$\overline{41}$
27	1	0	98	92	27	3	0	93	$\overline{89}$
29	1	0	158	$\overline{135}$	29	3	0	122	144
31	1	0	157	$\overline{131}$	31	3	0	146	142
33	1	0	87	75	33	3	0	79	$\overline{72}$
35	1	0	<26	10	35	3	0	<28	12
37	1	0	26	25	37	3	0	49	$\overline{53}$
39	1	0	39	29	39	3	0	51	$\overline{50}$
41	1	0	<28	$\overline{29}$	41	3	0	31	40
43	1	0	40	$\overline{37}$	43	3	0	31	44
45	1	0	42	44	45	3	0	54	$\overline{50}$
47	1	0	43	40	47	3	0	45	$\overline{43}$

With the help of these formulae, some structure factors have been computed from the unpublished data of Jain, Tavale & Biswas (see Appendix). These are compared in Table 1 with the observed structure factors. F_o were obtained from visually estimated intensities (after being corrected for the Lp factor); the scaling was done with the help of F_c. The agreement between F_o and F_c shows that the postulated structure of the polytype is correct.

The only other possibility of having a polytype from *A* and *B* layers with an *a* axial length which is twice that of the normal cell, is to have a structure with three layers of one type and the fourth layer of the other type, say *AAAB*; the other alternatives like *AABA*, *BBBA*, *etc.* may be obtained from *AAAB* by suitably changing the origin. However, this possibility is ruled out since for this structure, $F(Hk0)$ for k odd and $H=4n$ are, in general, present whereas such reflexions are actually found to be systematically absent (Fig. 2). As a further check, the intensity of the 28,1,0 reflexion was computed for this structure and was found to be more than the intensity of the 27,1,0 reflexion; however, in Fig. 2(*a*), the 27,1,0 reflexion can be clearly seen whereas 28,1,0 is absent.

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APPENDIX

BY S.C. JAIN, S.S. TAVALE & A.B. BISWAS

Atomic and thermal parameters in the basic structure

	x	*y*	*z*	*B*
Na	0·2215	0·2195	−0·0064	3·1 Å²
O(1)	0·2230	0·1563	0·3830	2·4
O(2)	0·1639	0·1592	0·1692	3·7
O(3)	0·2015	0·3802	0·6519	3·0
C(1)	0·2016	0·2492	0·4873	3·0
C(2)	0·1652	0·2235	0·3516	3·3
C(3)	0·1343	0·3083	0·4888	3·7
C(4)	0·1022	0·2066	0·3712	4·0
C(5)	0·0709	0·3156	0·5206	4·5
C(6)	0·0375	0·1944	0·4091	4·8