Polytypism in Potassium Cobalticyanide*

By J. A. Kohn and William D. Townes

U.S. Army Signal Research and Development Laboratory, Fort Monmouth, New Jersey, U.S.A.

Pure and doped (0·1% Cr) crystals of $K_3Co(CN)_6$, grown from aqueous solution, were examined by single-crystal X-ray methods. Four structural types were observed: Two-layer orthorhombic, and one-, three-, and seven-layer monoclinic, the latter two being new. The cells are related by stacking of (100) one-layer monoclinic lamellae; the mechanism, indicated from space-group considerations, is one of rotation about c and stacking on (100). The geometrical relationships demonstrate polytypism in this complex cyanide.

Morphological data and cell dimensions are given. Systematic extinctions other than space-group absences are explained. The 'cell twinning' of polytypism is discussed in contrast with 'twinning of crystals'.

Introduction

Interest in Cr-doped potassium cobalticyanide

$$(K_3Co(CN)_6)$$
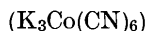
as a single-crystal, dilute paramagnetic salt for use in solid state MASER (microwave amplification by stimulated emission of radiation) application has prompted crystallographic studies of the substance.

Crystal growth

Pure and doped (0·1% Cr; established by spectrochemical analysis) crystals of $K_3Co(CN)_6$ were prepared by the following procedures: The starting materials, for pure crystals, were $CoCl_2.6\ H_2O$ and KCN, both reagent grade chemicals. Intermediate steps involved the formation of $Co(CN)_2$ and $K_4Co(CN)_6$. The latter was converted to a solution of the desired compound, and the final crystals were obtained by precipitation in a vacuum desiccator for a period of 6–8 weeks.

In order to obtain crystals doped with Cr, it was first necessary to prepare $K_3Cr(CN)_6$ from $CrCl_3$ and KCN as starting materials. Crystals of the Cr complex cyanide were crushed and added in required amounts to the $K_3Co(CN)_6$ solution before final precipitation. A detailed description of these crystal-growth procedures is given in a separate paper (Bramhall *et al.*, 1959).

Crystal morphology

Crystals obtained by the method described above were transparent, pale yellow-green. Doubly terminated prismatic and lath habits were observed. Single-crystal X-ray studies (see Unit Cell and Space Group) revealed four different structural types, apparently independent of doping (0·1% Cr) and with the same

morphology. For reasons discussed below, these are described by polytypic nomenclature (Ramsdell, 1947) as $1M$ (one-layer monoclinic), $2Or$ (two-layer orthorhombic), $3M$ (three-layer monoclinic), and $7M$ (seven-layer monoclinic). In each case, c was taken parallel to the length of the crystal, which ranged from 1 mm. to 2 cm. Forms observed on crystals of the four varieties are given in Table 1; spatially equivalent forms are grouped horizontally. Observed interfacial angles agree well with those calculated from cell dimensions obtained from single crystals.

Table 1. *Morphological data: Forms observed*

$2Or$	$1M$	$3M$	$7M$
(3 doped xls. / 2 pure xls.)	(2 doped xls. / 2 pure xls.)	(2 doped xls.)	(1 pure xl.)
100 (8)*	100 (5)	100 (4)	100 (2)
13,3,0 (2)	13,6,0 (2)		
210 (2)			
110 (17)	120 (16)	320 (2)	720 (3)
340 (1)			
322 (2)	$\bar{1}$11 (2)		
111 (10)	{ 144 (7) / 344 (7) }		$\overline{2}\bar{1}$,4,4 (3)
		$\overline{2}$11 (2)	
			111 (2)
122 (8)	{ 011 (4)	011 (2)	011 (2)
			$\overline{7}22$ (2)
011 (2)	$\bar{1}$44 (2)		$\overline{7}44$ (3)

* Figures in parentheses indicate numbers of faces observed.

All crystals were examined with a polarizing microscope, between crossed Nicol prisms. When viewed on (100), extinction was observed, as required, parallel to the traces of (010) and (001) in each case. Monoclinic crystals viewed on the major prism face (cf. Table 1) demonstrated extinction pseudo-parallel to the trace of (100), thus behaving optically pseudo-orthorhombic. In unpolarized light, several crystals showed fine, surface striations parallel to the trace of (100) on both prism and pyramid faces, this being manifest of a lamellar structure parallel to (100).

Table 2. *Historical summary*

Authors / Compound	Gottfried & Nagelschmidt (1930)	Büssem & Gottfried (1933)	Barkhatov & Zhdanov (1942)	Okaya & Pepinsky* (1956)	Okaya et al*. (1957)	Kohn & Townes (1961)
$K_3Fe(CN)_6$	$P2_1/c$ $\beta \sim 90°$†		$P2_1/c$ $\beta \sim 107°$		$Pnca$	
a	13·45‡		$\sim$ 7·1		13·45	
b	10·42		$\sim$ 10·4		10·43	
c; Z	8·40; 4		$\sim$ 8·4; 2		8·40; 4	
$K_3Cr(CN)_6$	$Pnca$				$Pnca$	
a	13·58				13·58	
b	10·62				10·62	
c; Z	8·62; 4				8·62; 4	
$K_3Mn(CN)_6$	$Pnca$				$Pnca$	
a	13·59				13·59	
b	10·62				10·62	
c; Z	8·52; 4				8·52; 4	
$K_3Ir(CN)_6$	$Pnca$					
a	13·73					
b	10·55					
c; Z	8·36; 4					
$Rb_3Fe(CN)_6$		$P2_1/c$ $\beta \sim 90°$†	$P2_1/c$ $\beta \sim 107°$			
a		13·77	$\sim$ 7·2			
b		10·68	$\sim$ 10·7			
c; Z		8·65; 4	$\sim$ 8·7; 2			
$K_3Co(CN)_6$			$P2_1/c$ $\beta = 107°$ 20'	$Pnca$	$Pnca$	$P2_1/c$ $\beta = 107°$ 19'
a			7·1	13·26	13·53	$Pnca$
b			10·4	10·53	10·50	Polytypes
c; Z			8·4; 2	8·32; 4	8·40; 4	(cf. Table 3)

* Settings transformed for comparison purposes.   † Results in error; refer to text.
‡ All dimensions in, or converted to Ångströms.

Unit cell and space group

A review of the crystallographic literature on $K_3Co(CN)_6$ and closely related compounds shows a considerably confused situation. Table 2 summarizes the results of various workers. Most of the confusion stems from the original work on $K_3Fe(CN)_6$ (Gottfried & Nagelschmidt, 1930) and $Rb_3Fe(CN)_6$ (Büssem & Gottfried, 1933). Although these phases were accurately described as monoclinic, pseudo-orthorhombic, erroneous a dimensions were given. The more simple, monoclinic cell, derived by Barkhatov & Zhdanov (1942) for isostructural $K_3Co(CN)_6$, is shown in Fig. 1 (left). They showed that pseudo-orthorhombic a is equal to 4·monoclinic $a \cdot \sin \beta \sim 27$ Å, this being twice the erroneous dimension given by Gottfried & Nagelschmidt and Büssem & Gottfried. The error apparently derives from scattering mass similarities at sites A and B in Fig. 1 (left).

It is unfortunate that the incorrect, pseudo-orthorhombic cells are almost identical in dimensions with their corresponding, rigorously orthorhombic, two-layer structures (Fig. 1, right). This fact has effectively hidden the presence of polytypism in such complex cyanides and caused several workers to accept the validity of these early results while refuting more recent, accurate studies. Okaya & Pepinsky (1956), for example, regarded the monoclinic cell given by Barkhatov & Zhdanov as erroneous, stating that 'disorder probably accounts for the incorrect symmetries reported . . .'.
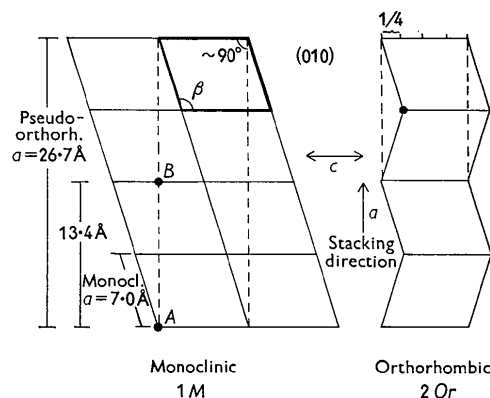

Fig. 1. Relationship of the $1M$ (one-layer monoclinic) and $2Or$ (two-layer orthorhombic) cells, as seen on (010). Note pseudo-orthorhombic cell for $1M$.

In the present X-ray study, lath-shaped and prismatic, doped and pure crystals of $K_3Co(CN)_6$ were examined by Weissenberg and precession methods, using Mo K and Co K radiation. Both the monoclinic cell of Barkhatov & Zhdanov ($1M$) and the orthorhombic cell reported by Okaya & Pepinsky ($2Or$) were found. Two additional monoclinic cells were also observed, these being three and seven layers thick along a^*, relative to the original (one-layer) monoclinic cell. Data for the four observed cells are summarized in Table 3.

The four cells thus far observed are obviously very

Table 3. *Unit-cell data for* $K_3Co(CN)_6$

	2Or	1M	3M	7M
a	13.31 ± 0.04 Å*	7.00 ± 0.02 Å	21.00 ± 0.06 Å	49.00 ± 0.15 Å
b	10.37 ± 0.02	10.38 ± 0.01	10.38 ± 0.01	10.38 ± 0.01
c	8.35 ± 0.01	8.37 ± 0.02	8.37 ± 0.02	8.37 ± 0.02
β	—	$107° 19 \pm 3'$	$107° 19 \pm 3'$	$107° 19 \pm 3'$
Z	4	2	6	14
Sp. gr.	$Pnca$	$P2_1/c$	$P2_1/c$	$P2_1/c$

* The conventional setting (Donnay & Nowacki, 1954) is not followed in order to show more clearly the relationship among the cells.

closely related. The geometry of the one-layer monoclinic and two-layer orthorhombic cells is shown in Fig. 1. It can be seen that $a_{2Or} = 2 \sin \beta \cdot a_{1M}$. The orthorhombic cell is geometrically derived from the monoclinic by alternate stacking (1·1) of $1M$ layers on (100). The stacking geometry is described in more detail below (see Stacking mechanism). Fig. 2 shows the geometrical derivation of the $3M$ cell from $1M$. This is accomplished by a 2·1 stacking on (100). Note that, owing to the pseudo-orthorhombic symmetry of the $1M$ lattice, $\beta_{1M} = \beta_{3M}$. Whereas, in the case of $3M$, there is but one possible stacking sequence, the $7M$ cell can be constructed with eight different stacking sequences.† The stacking relationships among
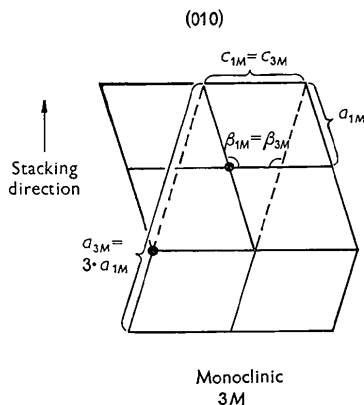

(010)

Fig. 2. Relationship of the $1M$ (one-layer monoclinic) and $3M$ (three-layer monoclinic) cells, as seen on (010).

the four cells demonstrate the phenomenon of polytypism in $K_3Co(CN)_6$.

Three-dimensional diffraction data were obtained for each structural type. Precession $(h1l)$ patterns, however, proved clearest for demonstrating the layering and discriminating among the various polytypes. Fig. 3 shows representative portions of the $(h1l)$ patterns for each of the four types. The a^*c^* nets depicted are identical in area. One can clearly see that $a_{1M}^* = 2a_{2Or}^* = 3a_{3M}^* = 7a_{7M}^*$.

Diffraction patterns from the two-layer orthorhombic type showed, in addition to the systematic

† Selection of the correct stacking sequence will be incidental to structure determinations on the new polytypes, forming the subject of another paper.

absences deriving from the space group $Pnca$, other absences as follows:

$$h_{2m+1}kl_{4n},$$

$$h_{2m}kl_{4n+2}.$$

Equivalent extinctions were also noted by Okaya & Pepinsky. These absences can be correlated with the 'lattice point' introduced at $\frac{1}{2}, 0, \frac{1}{4}$ by alternate stacking of $1M$ layers on (100) (cf. Fig. 1, right). Similarly, $3M$ diffraction patterns showed systematic extinctions over and above the space group $(P2_1/c)$ absences:

$$h_{3m\pm1}kl_{2n}.$$

These are explained by the 'lattice points' at $\frac{1}{3}, 0, \frac{1}{2}$ and $\frac{2}{3}, 0, 0$, introduced by virtue of the 2·1 stacking of $1M$ layers as shown in Fig. 2.

Stacking mechanism

Stacking customarily implies a random or systematic rotation of layers about their normal, i.e., about the *stacking direction*, as typified by SiC and ZnS. This does not appear to be the case, however, for $K_3Co(CN)_6$. Here the (100) stacking layers, instead of rotating about the stacking direction, are rotated about a vector *normal* thereto, namely c. Evidence for such a conclusion derives from space-group considerations.

In Fig. 4, a $1M$ cell having the space group $P2_1/c$ is rotated 180° about c and stacked on (100) to give a $2Or$ cell. The resultant two-layer orthorhombic cell has the space group $Pnca$, in agreement with the space group observed for the $2Or$ polytype. On the other hand, if the same $P2_1/c$ cell is operated upon by a rotation of 180° around the stacking vector, it can be shown that the resultant orthorhombic space group is $Pmcn$. The latter conflicts with observed symmetry and refers to the first mechanism as the correct stacking device.

The $3M$ cell presents more of a problem in this respect. A similar approach shows that both stacking mechanisms operating upon $1M$ $P2_1/c$ to give a $3M$ cell (Fig. 2) result in the same space group, $P2_1/c$. An unequivocal solution will develop only from the structure determination (see footnote p. 619). Similar arguments apply also to the $7M$ cell.

Barkhatov (1942) located the K^+ and Co^{3+} ions in the $1M$ polytype and inferred general $(CN)^-$ positions
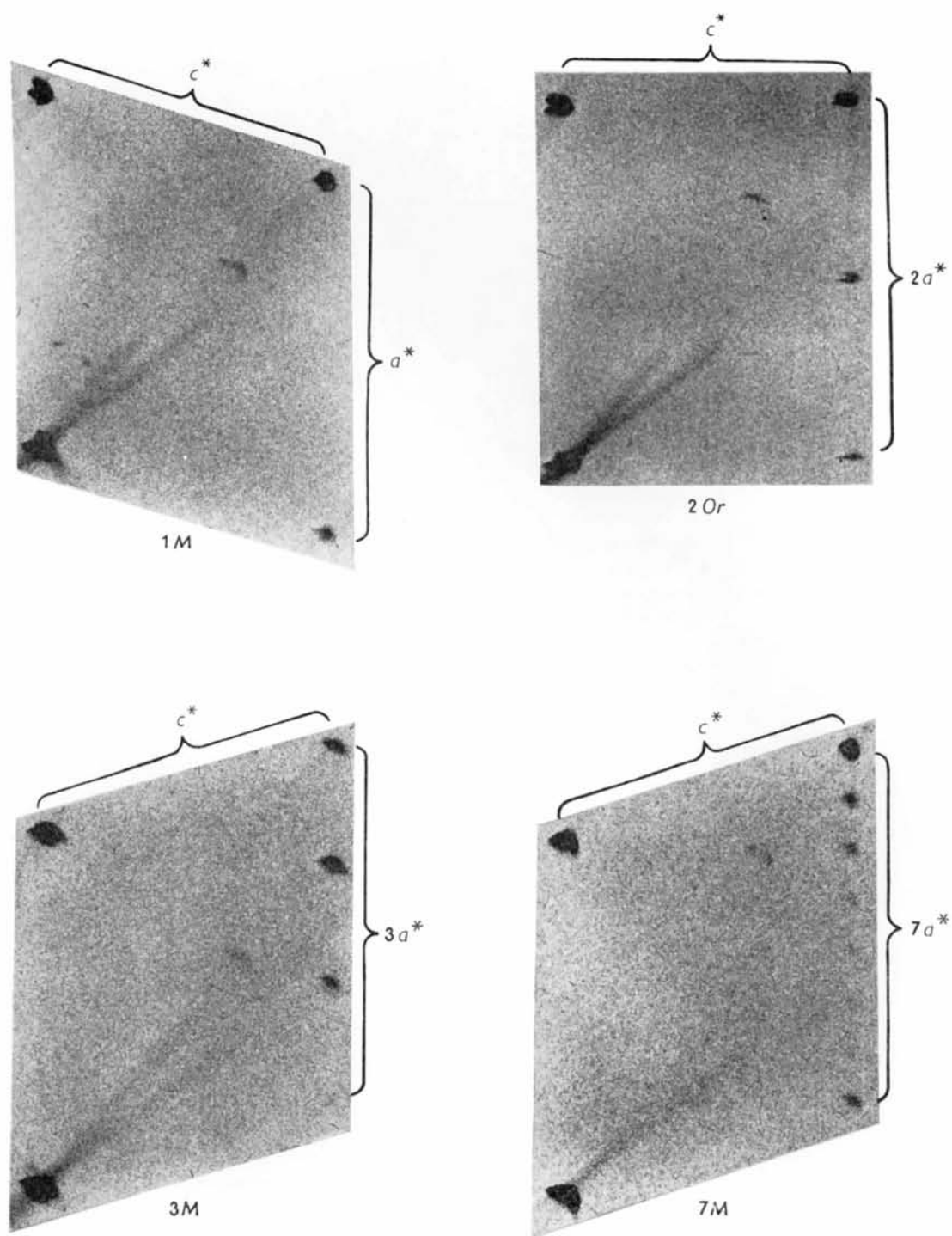
Fig. 3. Equivalent, representative portions of $(h1l)$ precession patterns for the $1M$, $2Or$, $3M$, and $7M$ polytypes; Co K, 30–40 hr. ($4 \times$, relative to the standard precession film).

Fig. 3. Equivalent, representative portions of (h1l) precession patterns for the 1M, 2Or, 3M, and 7M polytypes; Co K, 30–40 hr. (4×, relative to the standard precession film).
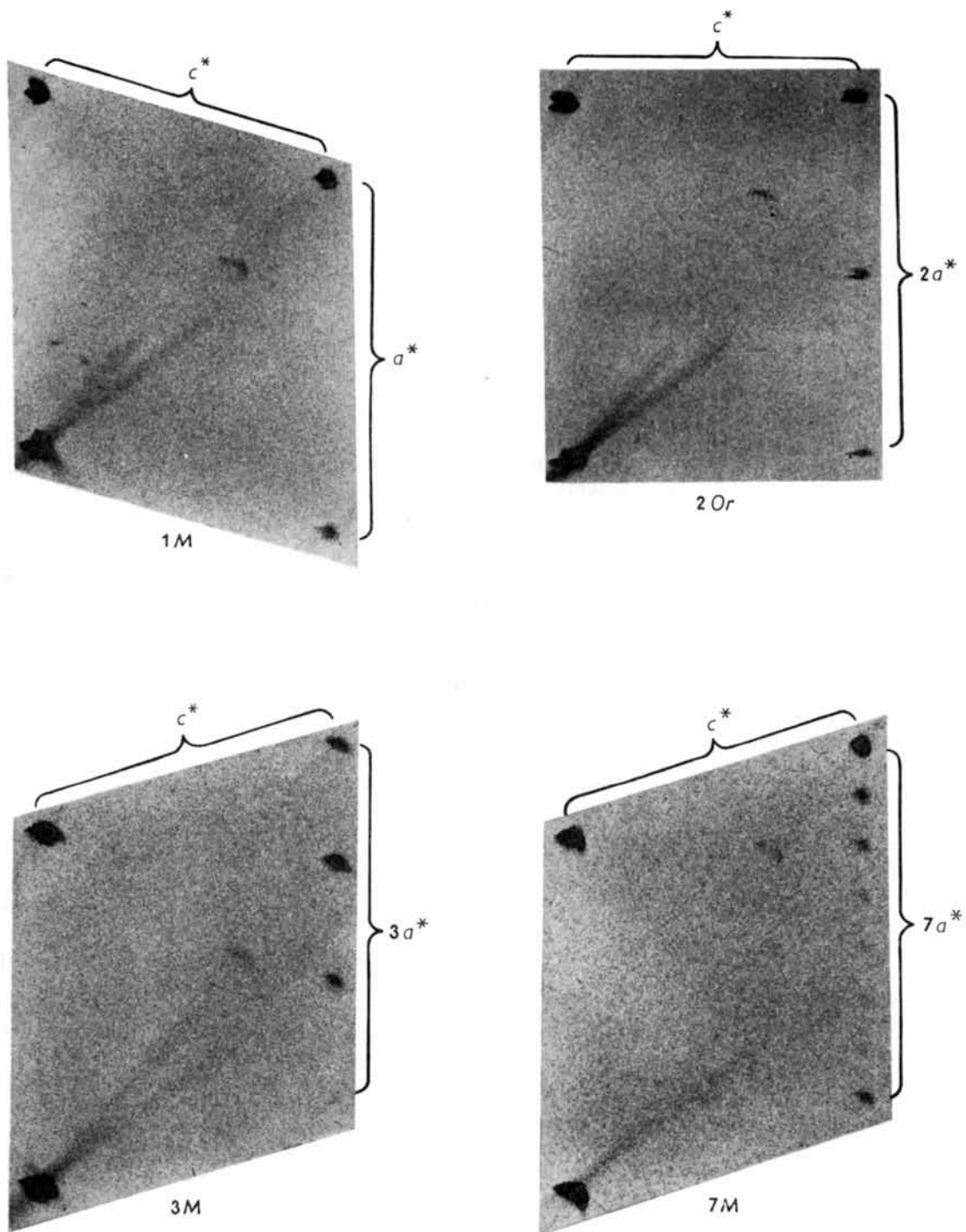
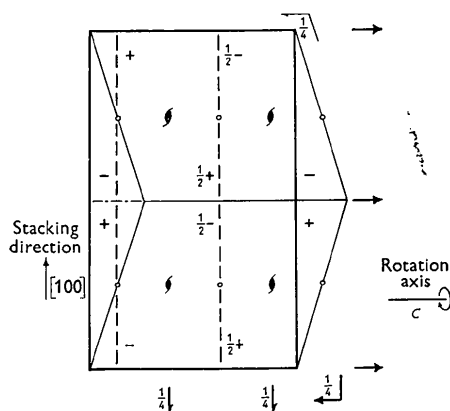Fig. 4. Derivation of Pnca (2Or) from P2₁/c (1M) by rotation around c and stacking on (100).

from spatial considerations. Recently, Curry & Runciman (1959) refined the 1M structure by neutron diffraction, confirming the 'main features' of Barkhatov's structure and locating the carbon and nitrogen positions (two alternative sets). Okaya & Pepinsky determined the structure of the orthorhombic polytype. They noted one-dimensional disorder in the form of diffuse streaks linking l-odd reflections parallel to a^*, with integral k indices. An explanation for the disorder was given on the basis of their structure. Their arrangement, relative to Barkhatov's configuration for 1M, is consistent with the stacking mechanism proposed herein and refutes the more normal stacking device.

Discussion

The ever-growing list of crystalline materials displaying polytypism, beginning with the prototype SiC and including ZnS, mica, CdI_2, etc., is extended to include the complex salt $K_3Co(CN)_6$. It takes little imagination to predict that many more crystalline materials will show this phenomenon when sufficiently detailed X-ray studies are conducted. A likely prospect is $K_3Fe(CN)_6$, since a cell of the 1M type was given by Barkhatov & Zhdanov and one of the 2Or variety by Okaya et al. An obvious hunting ground for seekers of polytypes is in tetrahedral structures having polymorphs analogous to wurtzite and sphalerite, especially if they wish to delve into the many possible solid solution series. It would not be surprising to find such systems replete with structures having the peculiarly repetitive 'cell twinning' inherent in polytypism.

Ito (1950) has studied various groups of polymorphous phases, showing that in several cases the rela-

tionship is one of repetitive 'twinning' of cells. The structures derived by virtue of this 'cell twinning' are termed 'polysymmetric', their symmetries being described by a 'twinned space group'. Such 'twinning of cells' is differentiated from 'twinning of structures', in which sense twinning is most commonly used. They can both be described by the same operations of geometry, but their diffraction effects are different: 'Structure twinning' gives additive diffraction effects; 'cell twinning' yields diffraction results definitive of a new, distinctive lattice. $K_3Co(CN)_6$ is an excellent case in point bearing upon Ito's studies. 'Structure twinning' is shown by a 1M crystal twinned on (100) to give a diffraction pattern which is seemingly orthorhombic but actually derives from two twin-related 1M lattices. The pure 2Or polytype, on the other hand, gives a pattern which is strictly orthorhombic, developing from 'cell twinning' of 1M on (100) via a 1·1 stacking sequence. $K_3Co(CN)_6$ in particular, and polytypic structures in general, present clear evidence for the usefulness of the concepts of 'cell twinning' and 'twinned space groups' in crystallography.

References

BARKHATOV, V. (1942). Acta Phys.-chim. URSS, 16, 123–4.

BARKHATOV, V. & ZHDANOV, H. (1942). Acta Phys.-chim. URSS, 16, 43–58.

BRAMHALL, P., GAULÉ, G. & WOLFF, G. (1959). Paper presented at Second Army Science Conference, West Point, N.Y.

BÜSSEM, W. & GOTTFRIED, C. (1933). Z. Kristallogr. 84, 317–8.

CURRY, N. A. & RUNCIMAN, W. A. (1959). Acta Cryst. 12, 674–8.

DONNAY, J. D. H. & NOWACKI, WERNER (1954). Crystal Data. New York: Geological Society of America, Memoir, 60, 138.

GOTTFRIED, C. & NAGELSCHMIDT, J. G. (1930). Z. Kristallogr. 73, 357–64.

ITO, T. (1950). X-ray Studies on Polymorphism. Tokyo: Maruzen.

OKAYA, Y. & PEPINSKY, R. (1956). Abstract of paper (I–6) presented at meeting of Amer. Crystallographic Assoc., French Lick, Indiana.

OKAYA, Y., PEPINSKY, R., TAKEUCHI, Y., KUROYA, H., SHIMADA, A., GALLITELLI, P., STEMPLE, N. & BEEVERS, A. (1957). Acta Cryst. 10, 798–801. Abstract of paper (7·15) presented at Fourth International Congress of International Union of Crystallography, Montreal, Canada.

RAMSDELL, L. S. (1947). Amer. Min. 32, 64–82.