

Studies in Domain Crystallography. II. A New Low-Temperature Crystal Structure of Potassium Cyanide

BY G. S. PARRY

Department of Chemical Engineering and Chemical Technology, Imperial College of Science and Technology, London, S.W. 7, England

(Received 2 August 1961)

The new low-temperature form of potassium cyanide, which arises when a single crystal is subject to a composite temperature cycle (Cimino, Parry & Ubbelohde, *Proc. Roy. Soc., A*, 252, 445, 1959), has been shown to be monoclinic with cell dimensions:

$$a = 8.97, b = 4.53, c = 7.47 \text{ \AA}; \beta = 122^\circ 19'$$

and space group *Aa*. It is suggested that this new structure is an ordered form of the normal low-temperature form of rubidium cyanide and some tentative conclusions are reached regarding its structure.

During a recent study of the low-temperature transition of potassium cyanide (Cimino, Parry & Ubbelohde, 1959), it was found that when a single crystal, which had undergone the normal transformation cycle from cubic (*C*) to orthorhombic (*R*) and back to *C*, was immediately recooled without being allowed to warm up to room temperature, a new crystal structure (*I*) was formed. This structure was apparently stable over the temperature range from -108 to -115 °C. Only when the temperature was lowered further did the normal low-temperature form *R* begin to appear and even at a temperature of -120 °C. the hybrid crystal had still not transformed entirely to this form. As the new structure was never obtained when the crystal was allowed to warm up to room temperature between successive transformations, it was apparent that its occurrence was bound up in some way with changes in the physical state of the cubic crystal once it had completed a transformation cycle and that, whatever the nature of these changes, they could be removed if the crystal was annealed. Even so, it was by no means obvious why a new structure should be formed and the present work was undertaken in the hope that it would throw some light on this problem.

In the work referred to above, the structural changes within the crystal were followed mainly by forward transmission Laue photographs recorded with Mo radiation on a flat-plate camera. When this new phase was detected, some oscillation photographs were taken with the same experimental arrangement. Although it was established that this structure could be obtained from all the crystals of pure KCN that were examined, the photographs of one crystal showed only a selection of the reflexions present on photographs of other crystals. This indicated that the transformation symmetry (Parry, 1962, Part I) was lower than cubic, a result that had already been encountered in the normal transformation. In contrast to the state of

affairs in the normal transformation however, the restriction on the allowed domain orientations did not lead to a new set of orientation relations and as the photographs given by this crystal showed fewer reflexions they were better suited for detailed interpretation. The oscillation photographs taken of this 'hybrid' crystal covered an angular range $0-45^\circ$ about one 4-fold axis of the original cubic crystal from an initial position in which the X-ray beam was parallel to a second cubic 4-fold axis. All the photographs showed well defined layer lines, the splitting of reflexions being essentially confined to within these layer lines. This indicated that the orientation of the axis about which the crystal was oscillated had remained unchanged throughout the transformation. The presence of a unique axis of transformation symmetry suggested that this symmetry was tetragonal and in the following interpretation it is taken to be *4/mmm*, an assumption which led to no inconsistencies.

Preliminary interpretation of the oscillation photographs

The most significant feature of the oscillation photographs of the *I* form was the presence of superlattice reflexions. For the crystal selected for investigation, these reflexions were quite sharp despite the fact that reflexions derived from those originally present in the cubic phase were obviously split. This was taken to mean that only one reciprocal axis of the new cell was halved. A preliminary indexing of these superlattice reflexions was made on the basis of the original cubic reciprocal lattice. This showed that even allowing for small dimensional changes in the lattice, the superlattice reflexions must have fractional indices $h + \frac{1}{2}$, $k + \frac{1}{2}$, $l + \frac{1}{2}$; thus it was apparent that the halved reciprocal axis must be one member of the zone form

$\langle 111 \rangle_c^*$ in the original cubic reciprocal lattice. This axis was an obvious choice for one axis of the new reciprocal lattice and was designated $[a^*]_i$.†

Following this conclusion, attention was directed to the $(hhh)_I$ reflexions, which were found to consist of three components each with a different θ . One of these components, must have indices $(2h, 0, 0)_i$ but those for the others must be determined by trial. It was observed (see Fig. 3(b)) that on the photograph on which the $(hhh)_I$ reflexions appeared, there were two reflexions of very small ξ on the second (cubic) layer line which were symmetrically disposed about the line $\xi=0$. As the difference $\Delta\xi$ between these two reflexions was indistinguishable from that between the extreme reflexions of the $(222)_I$ triplet, it seemed probable that they were $(002)_I$ and could define the direction of the second reciprocal axis of the new cell $[c^*]_i$ which would lie near but not exactly parallel to the oscillation axis. If one of these two reflexions was indexed as $(002)_i$ then the other could be considered as $(00\bar{2})'_i$ from a domain related by the horizontal plane of interdomain symmetry. The two extreme reflexions of the $(222)_I$ triplet then indexed as $(400)_i$ and $(40\bar{4})'_i$ although at this stage it was not possible to decide which was which. To account for the fact that only one member of $(222)_I$ remained to be indexed, the third axis of the new reciprocal cell was chosen to be perpendicular to both of those already defined in order that both $(0kl)_i$ and $(0k\bar{l})'_i$ should have the same interplanar spacing. This meant that the third axis $[b^*]_i$ must be derived from some axis of the type $[110]_c^*$ in the cubic reciprocal lattice and the remaining reflexion of $(222)_I$ was taken as the superposition of $(022)_i$ and $(02\bar{2})'_i$. Thus the three reciprocal axes of the new phase as defined above suggest that its symmetry is monoclinic, being derived from the cubic reciprocal axes in the following way:

$$[111]_c^* \rightarrow [100]_i^*; [\bar{1}10]_c^* \rightarrow [010]_i^*; [001]_c^* \rightarrow [001]_i^*.$$

The orientation of these axes in the cubic reciprocal lattice is shown in Fig. 1.

Estimates of the reciprocal-cell dimensions were obtained by measurement of the $(333)_I$ triplet whose

† In what follows, a lower-case subscript will be used to refer to a particular orientation while an upper case subscript will refer to the complete assemblage of domain orientations into which the crystal has transformed. It will be convenient to use upper-case subscripts in conjunction with indices based on the original cubic unit cell to denote the component reflexions into which a cubic reflexion splits on transformation. Thus as the temperature is lowered $(222)_C \rightarrow (222)_I \neq (222)_i$.

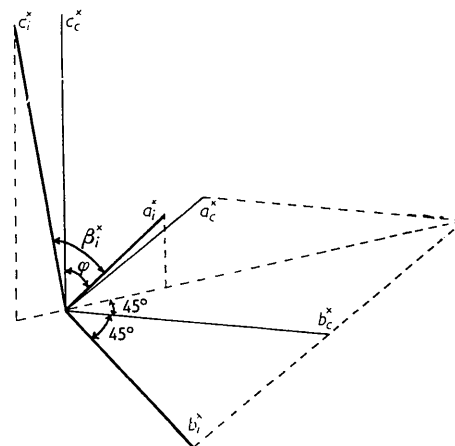


Fig. 1. The orientation of the reciprocal axes of the new low-temperature form of potassium cyanide, I, shown relative to those of the original cubic cell.

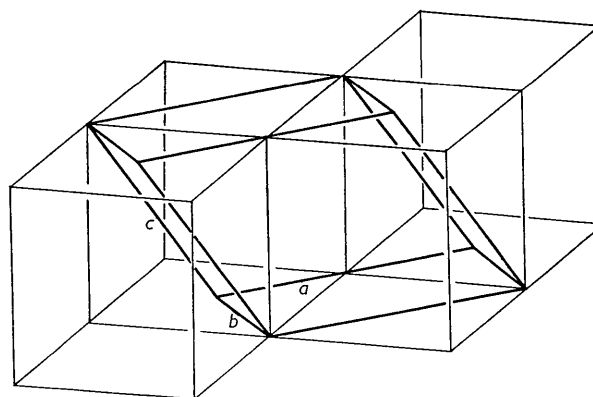


Fig. 2. The unit cell of the new low-temperature form of potassium cyanide shown relative to the original cubic lattice. The drawing is somewhat idealized; the slight dimensional and angular changes that occur on transformation have been ignored in the interests of clarity. The unit cell is in the same orientation as the reciprocal axes shown in Fig. 1.

components, although weak, were sharper than those of $(222)_I$. At this stage it was possible to choose the component with smallest ξ as $(600)_i$ because only in this way could the position of the superlattice reflexions be accounted for. The ξ, ζ coordinates of the component reflexions of $(333)_I$ are given in Table 1 in the form of equations which relate the observed numerical magnitude to analytical expressions involving five unknowns which specify both the new

Table 1. The coordinates of component reflexions

$(hkl)_i$	ξ	ζ
600	$6a_i^* \sin \varphi = 0.45$	$6a_i^* \cos \varphi = 0.336$
033	$3b_i^* = 0.475$	$3c_i^* \cos (\beta^* - \varphi) = 0.336$
606	$6[a_i^* \sin \varphi + c_i^* \sin (\beta^* - \varphi)] = 0.50_5$	$3c_i^* \cos (\beta^* - \varphi) = 0.336$

φ is the angle between c_c^* and a_i^* .

reciprocal cell and its orientation relative to the original cubic reciprocal lattice.

The equations given in Table 1 were solved to give the following values of the unknowns:

$$a_i^* = 0.094, \quad b_i^* = 0.157, \quad c_i^* = 0.112; \\ \beta^* = 57^\circ 51', \quad \varphi = 53^\circ 15'.$$

The dimensions of the corresponding cell in the space lattice are as follows:

$$a_i = 8.97, \quad b_i = 4.53, \quad c_i = 7.47 \text{ \AA}; \quad \beta_i^* = 122^\circ 19'.$$

A somewhat simplified drawing showing the way in which this cell is derived from the original cubic lattice is shown in Fig. 2.

Detailed interpretation of the oscillation photographs

Before the structural implications of this new cell are discussed, it is necessary to show that the above cell dimensions, which are based on the detailed interpretation of only a few reflexions on one diffraction photograph, do in fact account in detail for the distribution of reflexions in all the diffraction photographs. A method whereby the distribution of lattice points in the composite reciprocal lattice of a multi-domain crystal, which originate from a single reciprocal-lattice point of the original reciprocal lattice, can be derived has already been given in Part I and the same procedure will be followed here. It is convenient to choose the reference axes x, y, z of the original reciprocal lattice as follows:

$$x \parallel [110]_c^*; \quad y \parallel [\bar{1}10]_c^*; \quad z \parallel [001]_c^*$$

and to specify the orientation of these axes by the unit vectors \mathbf{u}_{110} , $\mathbf{u}_{\bar{1}10}$ and \mathbf{u}_{001} . These reference axes are convenient for the symmetry operations in the tetragonal point group of transformation symmetry, $4/mmm$, and also exhibit the $2/m$ symmetry which is preserved in the transformation,† a fact which simplifies the equations for the composite reciprocal lattice.

The general reciprocal lattice vector in the new lattice \mathbf{H}_i can be written:

$$\mathbf{H}_i = h_i \mathbf{a}_i^* + k_i \mathbf{b}_i^* + l_i \mathbf{c}_i^*$$

and the projections of this vector on to the standard axes are:

$$X = \mathbf{H}_i \cdot \mathbf{u}_{110}; \quad Y = \mathbf{H}_i \cdot \mathbf{u}_{\bar{1}10}; \quad Z = \mathbf{H}_i \cdot \mathbf{u}_{001}.$$

These scalar products are evaluated subject to the following conditions which arise from the mutual orientation of the initial and transformed lattices (see Fig. 1):

† It is assumed that $(010)_i \parallel (\bar{1}10)_c$, there being no evidence to the contrary.

$$\begin{aligned} \mathbf{a}_i^* \cdot \mathbf{u}_{110} &= a_i^* \sin \varphi, \quad \mathbf{b}_i^* \cdot \mathbf{u}_{110} = 0, \\ \mathbf{c}_i^* \cdot \mathbf{u}_{110} &= -c_i^* \sin(\beta^* - \varphi); \\ \mathbf{a}_i^* \cdot \mathbf{u}_{\bar{1}10} &= 0, \quad \mathbf{b}_i^* \cdot \mathbf{u}_{\bar{1}10} = b_i^*, \quad \mathbf{c}_i^* \cdot \mathbf{u}_{\bar{1}10} = 0; \\ \mathbf{a}_i^* \cdot \mathbf{u}_{001} &= a_i^* \cos \varphi, \quad \mathbf{b}_i^* \cdot \mathbf{u}_{001} = 0, \\ \mathbf{c}_i^* \cdot \mathbf{u}_{001} &= c_i^* \cos(\beta^* - \varphi) \end{aligned}$$

to give

$$\left. \begin{aligned} X &= h_i a_i^* \sin \varphi - l_i c_i^* \sin(\beta^* - \varphi) \\ Y &= k_i b_i^* \\ Z &= h_i a_i^* \cos \varphi + l_i c_i^* \cos(\beta^* - \varphi) \end{aligned} \right\} \quad (1)$$

To obtain the components XYZ for the other domain orientations thus giving the distribution of reciprocal-lattice points in the composite lattice, it is necessary to specify representative cubic reciprocal-lattice points which are related after transformation by elements of interdomain symmetry. The group $4/mmm$ has 16 general positions and the monoclinic symmetry preserved through the transformation, $2/m$ has only 4 general positions; hence it follows that there will be $16/4 = 4$ independent domain orientations. Thus only four cubic reciprocal lattice points are needed to specify all domain orientations after transformation. One such group of reciprocal-lattice points is given below, together with the symmetry operation (S) in the tetragonal point group (principal axes xyz) that relates each point to $hckcl_c$:

$$hckcl_c, (I); \quad \bar{h}ckcl_c, (m_{xy}); \quad \bar{k}chcl_c, (4^2); \quad \bar{k}_c \bar{h}cl_c, (m_x). \quad (2)$$

These indices must now be transformed into the new axial system by the equations

$$h_i = h_c + k_c; \quad k_i = -\frac{1}{2}h_c + \frac{1}{2}k_c; \quad l_i = -\frac{1}{2}h_c - \frac{1}{2}k_c + l_c$$

which gives the following values for $(hkl)_i$ in terms of the indices $(hkl)_c$

$$\left. \begin{aligned} h_c + k_c; & \quad -\frac{1}{2}h_c + \frac{1}{2}k_c; & \quad -\frac{1}{2}h_c - \frac{1}{2}k_c + l_c \\ -h_c + k_c; & \quad \frac{1}{2}h_c + \frac{1}{2}k_c; & \quad \frac{1}{2}h_c - \frac{1}{2}k_c + l_c \\ -k_c + h_c; & \quad \frac{1}{2}k_c + \frac{1}{2}h_c; & \quad \frac{1}{2}k_c - \frac{1}{2}h_c + l_c \\ -k_c - h_c; & \quad \frac{1}{2}k_c - \frac{1}{2}h_c; & \quad \frac{1}{2}k_c + \frac{1}{2}h_c + l_c \end{aligned} \right\} \quad (3)$$

When the indices $(hkl)_i$ given by (3) are inserted into (1), the components XYZ of the corresponding reciprocal-lattice vectors are obtained *within the standard domain*. To obtain the components $X'Y'Z'$ which fall in the same region of reciprocal space and so 'split' the original cubic reciprocal lattice point, each of these XYZ must now be operated upon by the appropriate symmetry operator S^{-1} to refer the components to a new domain orientation related by symmetry S^{-1} to the standard domain. The results, characterized by a letter n in the fourth column, are summarized in Table 2.

All indices $h_i k_i l_i$ given by equations (3) will necessarily have the index h_i as an even number, for the systematic absences of the cubic structure require h_c and k_c to be both even or both odd. Reflexions with h_i odd are the superlattice reflexions for which no

equivalent cubic reflexions exist. The equations so far derived in Table 2 do not therefore contain the superlattice reflexions. A systematic method of generating $X'Y'Z'$ for the superlattice reflexions is desirable however and can be derived in terms of a particular cubic reflexion as follows.

The cubic indices of the superlattice points can be obtained by adding $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$, to all cubic reciprocal-lattice points. The four equivalent cubic reflexions specified by (2) then become:

$$h_c + \frac{1}{2}, k_c + \frac{1}{2}, l_c + \frac{1}{2}; \quad -h_c + \frac{1}{2}, k_c + \frac{1}{2}, l_c + \frac{1}{2}; \\ -k_c + \frac{1}{2}, h_c + \frac{1}{2}, l_c + \frac{1}{2}; \quad -k_c + \frac{1}{2}, -h_c + \frac{1}{2}, l_c + \frac{1}{2}.$$

These indices can now be used to derive four equations specifying $X'Y'Z'$ for the superlattice points by the procedure outlined above; these equations are given in Table 2 opposite the entry denoted by the letter s in the fourth column.

All eight equations in Table 2 involve only the indices on one cubic reciprocal-lattice point so that by applying these equations systematically to each cubic reciprocal-lattice point in turn, the composite reciprocal lattice of the transformed crystal can be derived. In order to compare the calculated and observed reciprocal lattice coordinates it is necessary to convert the values of $X'Y'Z'$ obtained in this way into the normal reciprocal-lattice coordinates ξ, ζ , (which may be obtained from the photographs either by use of a Bernal Chart or by direct measurement) through the equations:

$$\xi = [(X')^2 + (Y')^2]^{\frac{1}{2}} \\ \zeta = Z'.$$

To test whether a particular reflexion with coordinates $X'Y'$ could occur within a given oscillation range it was found most convenient to use the normal graphical construction involving the two extreme positions of the reflecting circle, correctly oriented relative to the $X'Y'$ axes. The lack of complete resolutions of the 'split' reflexions on the photograph made a detailed comparison of observed and calculated impracticable but it was found that the appearance of a group of such reflexions was some times quite sensitive to the values of the parameters used to obtain X' and Y' . Hence the agreement between the observed and calculated positions of the component reflexions in any 'split' reflexion was judged by the overall appearance of the observed and calculated diffraction patterns; two such patterns are shown in Fig. 3(b), (c).

The positions of the superlattice reflexions, however, could be measured with reasonable accuracy and some results for the stronger reflexions lying on the first layer line of Fig. 3(b) are shown in Table 3. ξ_0 and ζ_0 were calculated from the positions of the reflexions as measured by a travelling microscope.

The agreement between the observed and calculated patterns shown in Fig. 3 and Table 3 was sufficiently good to be taken as confirmation that the cell dimen-

Table 2

Domain number	Interdomain symmetry S^{-1}	$X'Y'Z'$ $= S^{-1}(XYZ)$	Type of r.l.p.†	X'	Y'	Z'
1	I	XYZ	n	$(h+k)A_1 - (-\frac{1}{2}h - \frac{1}{2}k + l)C_1$	$(-\frac{1}{2}h + \frac{1}{2}k)B_1$	$(h+k)A_2 + (-\frac{1}{2}h - \frac{1}{2}k + l)C_2$
			s	$(h+k+1)A_1 - (-\frac{1}{2}h - \frac{1}{2}k + l)C_1$		$(h+k+1)A_2 + (-\frac{1}{2}h - \frac{1}{2}k + l)C_2$
2	m_{xy}	YXZ	n	$(\frac{1}{2}h + \frac{1}{2}k)B_1$	$(-h+k)A_1 + (\frac{1}{2}h - \frac{1}{2}k + l)C_1$	$(-h+k)A_2 + (\frac{1}{2}h - \frac{1}{2}k + l)C_2$
			s		$(-h+k+1)A_1 - (\frac{1}{2}h - \frac{1}{2}k + l)C_1$	$(-h+k+1)A_2 + (\frac{1}{2}h - \frac{1}{2}k + l)C_2$
3	4^1	$Y\bar{X}Z$	n	$(\frac{1}{2}h + \frac{1}{2}k)B_1$	$(-h+k)A_1 + (-\frac{1}{2}h + \frac{1}{2}k + l)C_1$	$(h-k)A_2 + (-\frac{1}{2}h + \frac{1}{2}k + l)C_2$
			s		$(-h+k-1)A_1 + (-\frac{1}{2}h + \frac{1}{2}k + l)C_1$	$(h-k+1)A_2 + (-\frac{1}{2}h + \frac{1}{2}k + l)C_2$
4	m_x	$\bar{X}YZ$	n	$(h+k)A_1 + (\frac{1}{2}h + \frac{1}{2}k + l)C_1$	$(-\frac{1}{2}h + \frac{1}{2}k)B_1$	$(-h-k)A_2 + (\frac{1}{2}h + \frac{1}{2}k + l)C_2$
			s	$(h+k-1)A_1 + (\frac{1}{2}h + \frac{1}{2}k + l)C_1$		$(-h-k+1)A_2 + (\frac{1}{2}h + \frac{1}{2}k + l)C_2$

† n : Transformed cubic r.l.p. s : Superlattice r.l.p.

$A_1 = a_1^* \sin \varphi$, $A_2 = a_2^* \cos \varphi$. $B_1 = b_1^*$. $C_1 = c_1^* \sin(\beta^* - \varphi)$, $C_2 = c_2^* \cos(\beta^* - \varphi)$.

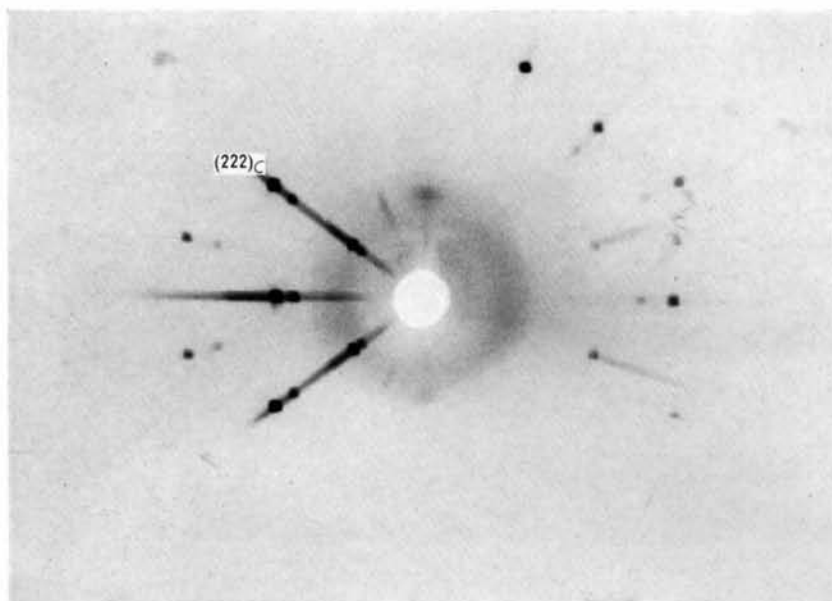


Fig. 3(a)

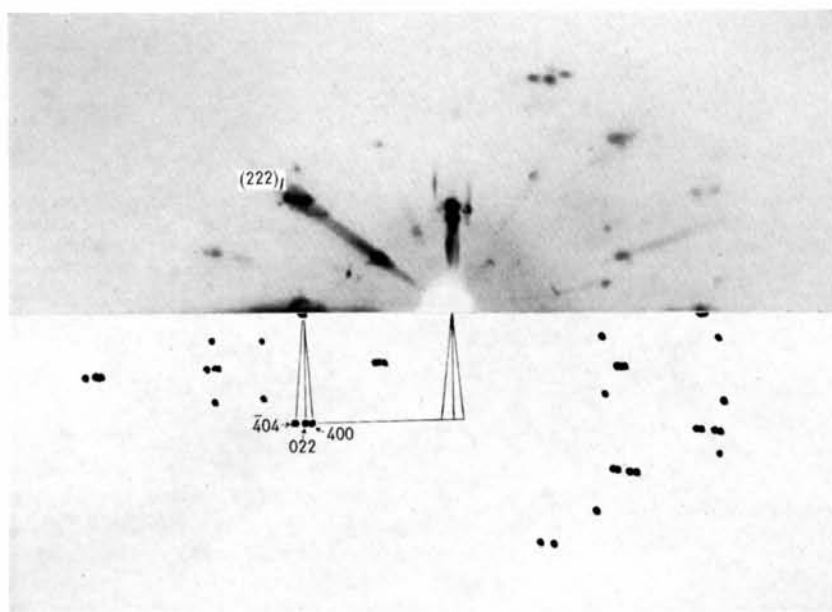


Fig 3(b)

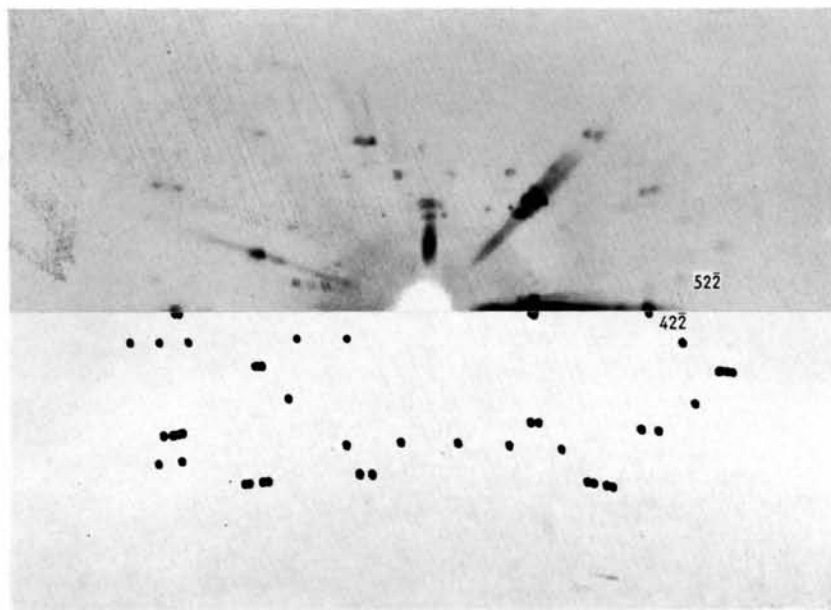


Fig. 3(c)

Fig. 3. A comparison of the calculated diffraction patterns with the experimental oscillation photographs. The oscillation photographs were taken with Mo K radiation on a flat film 4 cm. from the crystal. (a) Cubic crystal showing $(222)_c$. (b) I form showing splitting of $(222)_I$ which occurs after transformation. The indices on the calculated pattern refer to the true unit cell in various orientations. (c) I form rotated through 30° on the goniometer showing the reflexions $4\bar{2}\bar{2}$ and $5\bar{2}\bar{2}$ used to determine the y parameter of the potassium ion.

Table 3. *Positions of some superlattice reflexions*

Domain orientation	$(hkl)_i$	X'	Y'	Allowed limits of Y'		ξ_c	ζ_c	ξ_o	ζ_o
				Lower	Upper				
3	$52\bar{2}$	0.316	-0.393	-0.275	-1.457	0.504	0.056	0.495	0.057
3	$\bar{1}\bar{1}1$	-0.158	0.084	0.076	0.127	0.179	0.056	0.180	0.054
4	$3\bar{1}\bar{1}$	-0.234	0.158	0.100	0.178	0.282	0.056	0.281	0.055
2	$3\bar{3}\bar{1}$	-0.474	0.234	0.136	0.262	0.529	0.056	0.528	0.054

sions and orientation relations given earlier were essentially correct.

The space group and crystal structure

An examination of the indices of reflexions observed for any particular domain orientation showed that reflexions were present only for $k+l$ even, so that the lattice is A face centred. In addition, it was observed that reflexions of the type $h0l$ occurred only when h was even. These absences are consistent with the space groups Aa and $A2/a$. The calculated density, based on the observed cell dimensions,

$$a=8.97, b=4.53, c=7.47 \text{ \AA}; \beta=122^\circ 19',$$

and the assumption of four formula units KCN per unit cell, is 1.69 g.cm.^{-3} which can be compared with the calculated density of the cubic form just above the transition point of 1.63 g.cm.^{-3} and that of the normal low temperature form, 1.64 g.cm.^{-3} (*Structure Reports*, 1955). No significance is attached to the slight density increase in the new form as this is not outside experimental error. The calculated density merely served to confirm that there are four formula units in the unit cell of the new structure and that the space group must be Aa ; otherwise the carbon and nitrogen atoms would be in special positions that are structurally improbable.

It follows that all atoms are in positions of the type

$$xyz: x + \frac{1}{2}, \bar{y}, z: x, y + \frac{1}{2}, z + \frac{1}{2}: x + \frac{1}{2}, \frac{1}{2} - y, z + \frac{1}{2}.$$

and as the space group lacks a centre of symmetry, the x and z parameters of the potassium ion can be taken as zero, leaving only one parameter of the potassium ion to be determined. To a first approximation, the contribution of the cyanide group to the structure factors can be ignored and the expressions for the structure factor reduce to:

$$\begin{aligned} k+l \text{ even; } h \text{ even; } A &= 4f(\text{K}^+) \cos 2\pi ky(\text{K}^+), B=0; \\ h \text{ odd; } A &= 0, B = 4f(\text{K}^+) \sin 2\pi ky(\text{K}^+); \\ k+l \text{ odd; } A &= 0, B=0. \end{aligned}$$

Thus, in principle, an estimate of the magnitude of $\tan 2\pi ky(\text{K}^+)$ and so of $y(\text{K}^+)$ should be possible if the intensities of reflexions with h odd are compared with those with h even.

Difficulties arise in practice because as mentioned earlier the experimental arrangement for recording the

diffraction patterns does not give good resolution of diffraction spots with h even and, although this resolution could be improved by the use of a larger specimen-film distance and of a cylindrical film holder, this would involve a considerable increase in exposure time. Since this form of KCN is stable only over a temperature range of a few degrees, such exposures would require automatic control of the crystal temperature. A thermostat which it is hoped will enable such long exposures to be made is under construction but its absence in the present experiments meant that it was impracticable to obtain the parameter $y(\text{K}^+)$ with any precision.

On the other hand it was felt that it would be worth while to attempt to estimate at least the order of magnitude of $y(\text{K}^+)$ by using $(400)_i$ as the reflexion with h even, for this consists exclusively of $\{42\bar{2}\}_i$ and is therefore 'unsplit'. For comparison with this h even reflexion, a neighbouring superlattice reflexion $(52\bar{2})_i$ was selected. This occurs within the same oscillation range as $\{42\bar{2}\}_i$ and the difference in θ values for these two reflexions is small enough to enable the effects of temperature factor to be ignored. The intensities were recorded with Mo $K\alpha$ radiation using a pack of four flat films interleaved with aluminium foil. The two intensities were corrected for Lorentz-polarization factor, for the multiplicity of $\{42\bar{2}\}_i$ and for the difference in $f(\text{K}^+)$ between the two reflexions. The value of the $y(\text{K}^+)$ parameter obtained in this way was 0.24 \AA which was taken to imply that it was of the order of a few tenths of an Ångström.

In order to fill space adequately and to satisfy the charges on the potassium ions locally, the cyanide group must be centred on or near the point $\frac{1}{4}, 0, \frac{1}{2}$. According to Bijvoet & Lely (1940), the cyanide group can be adequately represented in the normal low-temperature form by an ellipse whose major and minor axes are 4.30 and 3.56 \AA respectively. Such an interpretation accounts for the contraction of one of the axes from 6.43 \AA in the cubic phase to 6.14 \AA in the normal low-temperature form, for the major axis of the ellipse was shown to be perpendicular to this direction. In the present case the equivalent repeat distance is 6.36 \AA ($\frac{1}{2}[102]_i$) so that, provided the cyanide group is still adequately represented by such an ellipse, its major axis must be inclined to $[102]_i$ at an angle very much less than 90° . A detailed calculation gives the angle as 51.5° which is surprisingly close to the angle between $[001]_c$ and $[111]_c$.

of the high-temperature form (54.7°) and suggests that the structure of this new form is based on a distorted cubic structure in which the major axis of the cyanide group is orientated along *one* of the body diagonals.

Certainly, this picture accounts for the distortion of the cubic cell dimensions which occur when this new modification appears. Thus $[111]_c$ and $[\bar{1}\bar{1}\bar{1}]_c$ whose repeat distance are both 11.14 \AA transform into two axes of different length (2×11.40 and $2 \times 10.85 \text{ \AA}$) and the larger of these, $[302]_i$ is inclined to $[102]_i$ at 51.6° which almost exactly equals the angle of tilt of the cyanide group deduced from the repeat distance of $[102]_i$.

However all this ignores the small displacements of the potassium ions which are an essential part of this new structure. Probably the cyanide group rotates so as to equalise the distances to the coordinating potassium ions. Merely to see whether the estimated value of $y(K^+)$ was sensitive to the inclusion of the cyanide-group contribution to the structure factors used in its estimation, the fractional coordinates of the C and N atoms were derived on the basis of the above assumption, (using a C-N distance of 1.1 \AA) and were found to be 0.25 ± 0.02 , ± 0.06 , 0.5 ± 0.04 . The change in the value of $y(K^+)$ after the cyanide contribution was included in the two structure factors was less than 0.01 \AA so that the assumption made earlier, namely that the potassium ion contribution predominates in these two structure factors, is valid.

Discussion

Although the atomic movements described above are unlikely to be quantitatively correct, they do nevertheless enable a qualitative picture of the structural changes that occur on transformation to be obtained. As would be expected from thermodynamic considerations, these structural changes arise because the cyanide groups are no longer positionally disordered as in the cubic phase. In the normal low-temperature form *R*, the cyanide groups assume parallel orientation and to accommodate the geometrical asymmetry of these groups, considerable dimensional distortions of the original cubic cell are required. In the new form *I*, assuming that the cyanide group is indeed rotated out of a position in which its major axis is parallel to $[302]_i$ there are two orientations of the cyanide group in the unit cell which result in the displacement of alternate sheets of potassium ions parallel to $(100)_i$ ($\approx (101)_c$) by an amount $\pm y$, where y is of the order of a few tenths of an Ångström. By means of these displacements, the distortions of the cubic structure are to a certain extent 'built in' to the unit cell of the new structure and as a result this unit cell involves less dimensional distortion of the original cubic cell than does the normal low-temperature form as is shown below:

	$a=c$	b	$\alpha=\gamma$	β
High temperature cubic form	6.43 \AA	6.43 \AA	90°	90°
Normal low temperature form <i>R</i>	6.61	6.14	90	101
New low temperature form <i>I</i>	2×6.43	2×6.36	$93\frac{1}{2}$	$90\frac{1}{2}$

In the normal low-temperature form the cyanide group is oriented with its major axis approximately parallel to the cubic axis $[110]_c$. In the new form this orientation changes to be more nearly parallel to $[111]_c$ and this change in orientation results in a change in the geometrical coordination of the cyanide group by the potassium ions. In form *R*, four potassium ions lie in a plane containing the C-N bond and the remaining two lie in a perpendicular bisector to that

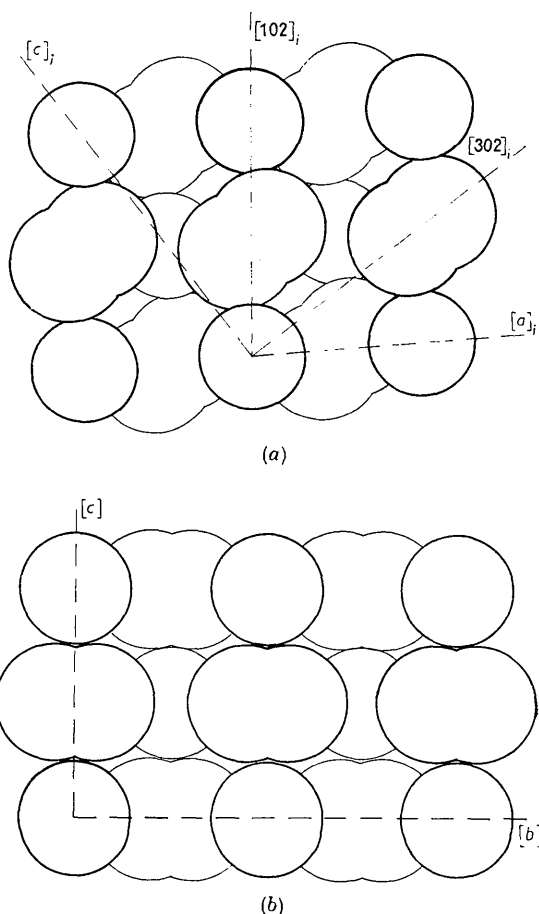


Fig. 4. (a) Proposed structure for the new low-temperature form of potassium cyanide projected on to $(010)_i$. The displacement $y(K^+)$ is perpendicular to the plane of this drawing and has been established experimentally to be of the order of $\frac{1}{4} \text{ \AA}$. The orientation of the cyanide group has not yet been experimentally confirmed but is based on a self-consistent interpretation of the cell dimensions, details of which are given in the text. (b) The normal low-temperature form *R* as found by Bijvoet & Lely, shown projected on to $(100)_r$. The equivalent planes of projection in the cubic crystal are both $(110)_c$.

bond. In the new form *I*, the C-N bond points towards the centroid of an equilateral triangle formed from three potassium ions, the two triangles at opposite ends of the cyanide group being in the staggered configuration. A drawing of the proposed structure for *I*, projected on to $(010)_i$ is shown in Fig. 4(a) and for comparison the structure *R* is shown projected on to the equivalent $(100)_r$ (Fig. 4(b)). Both planes of projection are approximately parallel to the cubic lattice plane $(101)_c$.

The discovery of a second low-temperature structure for KCN was quite unexpected and raised the question whether KCN is unique or whether other substances might behave in a similar way. An attempt to obtain this new structure from cubic NaCN (Cimino, 1960) was unsuccessful despite the fact that in all other respects the behaviour of NaCN on transformation is identical to that of KCN. It is now thought that the reason why KCN exhibits this behaviour has to do with the relative sizes of the potassium and cyanide ions. There is strong evidence that this new structure is related to that of the low-temperature form of RbCN which, as was found by Bijvoet & Lely (*Structure Reports*, 1955), is quite different from that of NaCN and KCN. In other words, it appears that KCN is dimorphic and that conditions favouring the nucleation of the second form can occur if the crystal is subjected to certain cycles of temperature variation.

In *Structure Reports* (1955) RbCN is referred to as pseudomonoclinic on the grounds that it was not possible to account for the observed intensities in detail on the basis of the monoclinic cell deduced from the X-ray diffraction photographs which had the following dimensions:

$$a = 4.78, b = 4.88, c = 6.67 \text{ \AA}; \beta = 94.5^\circ$$

and is oriented relative to the original cubic cell in such a way that *a* and *b* are derived from the semi-diagonals of one cube face and *c* from the cube edge perpendicular to that face. To obtain the corresponding unit cell from the lattice of the new KCN structure it is necessary to take

$$a = \frac{1}{2}[a]_i, c = \frac{1}{2}[102]_i,$$

which gives a 'unit cell' of the following dimensions

$$a = 4.45, b = 4.53, c = 6.36 \text{ \AA}; \beta = 94.6^\circ.$$

Comparing these dimensions with those of for RbCN, the difference in the axial lengths *a*, *b*, and *c* of the two cells are seen to be 0.28, 0.35 and 0.31 Å respectively. Since the cell dimensions are not necessarily very accurate, the average difference of 0.31 Å agrees well with the difference in ionic radii of potassium and rubidium of 0.3 Å (Pauling, 1948). Hence it would appear that the crystals of RbCN investigated by Bijvoet & Lely had, almost certainly, a disordered form of this new KCN structure in which the superlattice lines were not observable and that this superlattice structure is the more complicated cell which Bijvoet & Lely concluded must exist.

The reason why the RbCN structure is disordered is not clear. In cubic NaCN, the sodium atoms are probably randomly displaced in specific directions from their ideal positions in the cubic lattice in order to accommodate the cyanide groups (see *Structure Reports* (1955)) and similar displacements would be expected in the cubic form of RbCN. If this is so then the ordering of the Rb ions into a superlattice will be a more complex process than the mere displacement of alternate sheets of ions by $\pm y$ from their ideal positions in the cubic lattice. As the transition temperature of RbCN is lower than that for KCN, it may be that the energy of the Rb ions is insufficient for them to achieve this ordered superlattice. An alternative possibility is that the essential role of the preliminary transformation in the case of KCN is to reduce the disorder in the cubic phase. Whatever is the final answer to these questions, it is apparent that further work is desirable not only on this new structure for KCN but also on the low-temperature structure of RbCN and on the low-temperature behaviour of mixed salts of rubidium and potassium cyanide.

References

- BIJVOET, J. M. & LELY, J. A. (1940). *Rec. Trav. chim. Pays-Bas*, **59**, 908.
 CIMINO, A. (1960). Private Communication.
 CIMINO, A., PARRY, G. S. & UBBELOHDE, A. R. (1959). *Proc. Roy. Soc. A*, **252**, 445.
 PARRY, G. S. (1962). *Acta Cryst.* **15**, 596.
 PAULING, L. (1948). *The Nature of the Chemical Bond*. Ithaca: Cornell University Press.
Structure Reports (1955). Vol. **9**. Utrecht: N. V. A. Oosthoek's Uitgevers Mij.