

CRYSTAL STRUCTURE OF TRIPOTASSIUM CUPROCYANIDE

Thesis by
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Because there were inconsistencies in work of Cox, Wardlaw, and Webster done on the crystal structure of tripotassium cuprocyanide¹, it was thought that a new and more extensive investigation of the structure would be useful and interesting. It was proposed to attempt a complete structure determination, but, at this time, only the space group and one of four parameters have been determined.

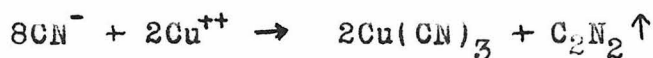
Cox, Wardlaw, and Webster say of potassium cuprocyanide, it "forms large rhombohedral crystals which, in view of their strong pyroelectric properties and the absence of vertical planes of symmetry (as shown by Laue photographs), must be assigned to the trapezohedral class (D_3)." They found two molecules per unit cell, and because of the trigonal axis and low birefringence of the crystals, they assume the cuprous tetracyanide complex to be tetrahedral. They report that the crystals form with $\{110\}$ faces predominant and occasional small $\{100\}$ faces. To quote, "the cell dimension is $a = 8.00\text{\AA}$ and $\alpha = 77^\circ 32'$. The number of molecules in the unit cell is 2, whence $d(\text{calc.}) = 2.06\text{g./cc.}$ (obs. 2.07)." The report has two errors, one of which may be real, and the other of which is probably a misprint. In the first case, Laue photographs cannot distinguish between point groups D_{3d} , D_3 , and C_{3v} . An X-ray experiment adds a center of symmetry as a result of the centrosymmetric character of X-ray diffraction, and the three mentioned point groups, by addition of a symmetry center, all become D_{3d} . Actually the point group will be shown to be C_{3v} . Furthermore, Laue symmetry D_{3d} , which they reported, shows vertical planes of symmetry -- not their absence.

The misprint occurs in the report on the cell dimensions.

A crystal with two molecules per unit in the cell given would have a density of 1.96g./cc. and it is probable that the α they found was about 74°.

In 1924, the phase diagram of the system KCN-CuCN-H₂O was investigated at 25°C. by Bassett and Corbet.² They found that only two complex salts could be recrystallized, K₃Cu(CN)₄ and K₃Cu(CN)₄·H₂O. The hydrated salt was reported to form large, colorless rhombohedra and the anhydrous salt to have "a more prismatic tendency". They said the hydrated crystals were metastable in contact with solution at 25°C. I crystallized tri-potassium cuprocyanide at 20°C. and at 40°C., and large, rhombohedral crystals formed at both temperatures. These crystals were, however, found to be anhydrous and there was no indication of the formation of hydrated salt.

Crystals of K₃Cu(CN)₄ were made according to the directions of Bassett and Corbet. A hot, aqueous solution of KCN was added slowly to a hot solution of copper sulfate, and paracyanogen formed was filtered out.



The resultant brown solution was slightly acidified with dilute sulfuric acid. A white, curdy precipitate of cuprous cyanide was formed and filtered out on a Buchner funnel. The precipitate was washed and then dried in a desiccator over calcium chloride. When saturated potassium cyanide solution was added to the dry precipitate, there was a vigorous evolution of gas and the temperature of the solution rose to about 80°C. This solution was filtered and allowed to evaporate. To prevent excess formation

of the paracyanogen, it might be better to add a mud of the CuCN to the solution of KCN in making the cuprocyanide and to use cold, dilute solutions in precipitation of the cuprous cyanide.

Recrystallization of the salt is necessary to get crystals well suited for analytical work, but, for crystallographic purposes, excessive purification is not desirable. The pure salt does not easily form perfect crystals, but tends to climb the sides of the dish and form porous masses of salt, and to form very large crystal aggregates on the bottom of the dish. Small crystals forming on the bottom were almost invariably shown to be split on X-ray examination, though they were superficially perfect. The crystal faces, though practically perfect in the solution, quickly deteriorated in the air as a result of the hygroscopic nature of the crystals. For goniometric measurements, it was necessary to put a drop of oil on each crystal, and even then the faces gradually roughened. Over a period of several days, the crystals would form small growths on the surface in spite of treatment with oil. The interior of the crystal underwent no apparent decomposition.

Single crystals formed as large colorless rhombohedra with the form $\{110\}$ predominant. Occasionally, faces of the form $\{100\}$ occurred, and very rarely a $\{111\}$ face was seen. The angles between $\{110\}$ faces were found to be $77^{\circ} 8'$ and $102^{\circ} 52'$ in the best set of measurements and, from this, the angle α' between edges

GONIOMETRIC MEASUREMENTS ON $\text{K}_3\text{Cu}(\text{CN})_4$
ROTATING THE CRYSTAL ABOUT $[110]$

				Mean	Difference
$303^{\circ} 2'$	$303^{\circ} 5'$	$303^{\circ} 6'$	$303^{\circ} 4'$	$77^{\circ} 8'$	
$20^{\circ} 10'$	$20^{\circ} 12'$	$20^{\circ} 14'$	$20^{\circ} 12'$	$102^{\circ} 51'$	
$123^{\circ} 0'$	$123^{\circ} 4'$	$123^{\circ} 6'$	$123^{\circ} 3'$	$77^{\circ} 8'$	
$200^{\circ} 9'$	$200^{\circ} 11'$	$200^{\circ} 12'$	$200^{\circ} 11'$	$102^{\circ} 53'$	

formed by the intersection of {110} faces was calculated to be $102^{\circ} 52'$. The rhombohedral angle, α , was then found by further calculation to be $74^{\circ} 14'$.

Several such large crystals, all about 0.1cc. in volume were collected and dried in a desiccator over calcium chloride for use in a density determination. The crystals were weighed in a pycnometer calibrated with water at room temperature; the pycnometer was then filled with machine oil and weighed; and finally the density of oil was determined in the same pycnometer. The weights used were not calibrated, and the temperature was not carefully controlled. The oil was of high viscosity, and minute air bubbles may have been trapped in the pile of crystals in excess of the amount in the oil itself. The crystals also very likely contained some included moisture. The density was found to be $1.99 \pm .10$ g/ml at 18°C . Cox found 2.07, which is within the limit of error of my determination and is also different in the direction indicated by my two chief sources of error, entrapped air and entrapped water.

The crystals were found to scratch rock salt and to be scratched by galena. The hardness was fixed at between 2.1 and 2.5 by a series of experiments and estimated at 2.4. Galena is listed as having hardness 2.5.³ The crystals scratch and are scratched by galena, though the galena seems slightly harder. Blue vitriol and the crystals have the same hardness and blue vitriol is scratched definitely by galena. Therefore, if galena has hardness 2.5, the crystals have a hardness of about 2.4.

Cox reported that the crystals were pyroelectric, and they are very strongly so. A crystal suspended on a thread and

dipped into a dewar of liquid air moves rapidly to the side and sticks there. The pyroelectricity is several times as strong as that of quartz. On removing ^{the crystal} ~~it~~ from liquid air, streamers of ice radiating from all corners of the crystal, including the corners with the three-fold axis, were observed and so the ends of the axis must have acquired a charge. The three-fold axis is, therefore, polar.

Cox, Wardlaw, and Webster described large, rhombohedral crystals of $K_3Cu(CN)_4$. Bassett and Corbet spoke of large, rhombohedral crystals of $K_3Cu(CN)_4 \cdot H_2O$. I got the large, rhombohedral crystals, but, to be sure of their composition, had to analyze them. Recrystallized $K_3Cu(CN)_4$ was separated from the mother liquor and allowed to dry for several days. The large crystals were separated from the small, and the floating from those on the bottom. In all, there were six samples. What was probably the best sample was set aside in case of mishap, and analyses were made on the other five. Each sample was washed once with a small quantity of distilled water and blotted dry with filter paper. They were dried overnight in a desiccator and for one half hour at $125^\circ C$. Three-quarter gram samples were weighed into five beakers. Each was dissolved in about 20ml. of water, 15 ml. of 0.546N H_2SO_4 were added, and the solution allowed to stand overnight. Next day, the white precipitate was filtered out on sintered glass crucibles and washed four to six times with a total of about 25 ml. of water each. The precipitate was dried at $130^\circ C$ for two and one half hours and weighed. (Another half hour of drying did not change the weight appreciably.) The filtrate was titrated with half normal sodium hydroxide using

methyl orange as indicator, and the alkali content of the crystals thus determined. Assuming KCN, CuCN, and H₂O to be the only possible constituents, the analysis averaged 69.89% KCN and 30.42% CuCN. (Calculated for K₃Cu(CN)₄, 68.59% and 31.45%, for K₃Cu(CN)₄·H₂O, 64.47% and 29.59%) In one analysis, (results discarded) after the back titration and several hours' standing, a greenish precipitate (Cu(OH)₂?) was observed. Since acid dissolves CuCN also, it is probable that CuCN precipitation was not complete in any sample. The analysis was probably good to 2% in the case of CuCN and to 1% in the case of the alkali determination. An impurity such as KOH formed by loss of HCN on drying, or of KCN from the mother liquor would cause variations from the calculated percentages such as are observed.

RESULTS OF ANALYSES

Sample	Weight	ml. NaOH	ml. H ₂ SO ₄ used	Meq H ⁺ = meq KCN	Wt. KCN	%KCN
#1	.7232	0.735	14.18	7.740	.5040	69.69
#2	.7354	0.525	14.39	7.855	.5116	69.59
#3	.7088	0.88	14.035	7.664	.4992	70.40

Sample	Wt. CuCN	%CuCN
#1	.2187	30.41
#2	.2238	30.43
#3	.2158	30.43

X-ray determination of a crystal structure depends on the fact that a crystal acts as a three dimensional grating, diffracting electromagnetic X-radiation. The intensity of diffraction in various directions depends in a definite manner on the nature of the spacings in the grating, or on its lattice structure, and on the nature of the points in the grating, or the arrangement of matter about the points of the lattice. Because there are but a definite number, fourteen, of possible lattices, it is possible to determine directly in a straightforward manner on which of these lattices the crystal is based. All possible combinations of all the conceivable symmetry elements result in only two hundred and thirty such combinations, which are called space groups, and, in a straightforward manner, it is possible to distinguish almost all of these space groups from each other. Exceptions are enantiomorphic space groups, which cannot yet be distinguished, and two special pair of isomorphous space groups which have the same symmetry elements in different translational arrangement.

To find the arrangement of matter around a lattice point is not so straightforward and not always as simple. When the arrangement is fairly complicated, the problem is analogous to that of solving n equations with m unknowns. The m unknowns represent the arrangement of the matter, and the n equations, the observations of direction and intensity of diffracted beams of X-rays. What makes the problem hard is that the equations are not simple, but are sums of sines and cosines of combinations of the unknowns. However, specific problems may be simplified by using knowledge gained from stereochemistry, complex formation, and studies of similar structures.

A crystal grating may be regarded as a system of points sending out electromagnetic radiation from each point as that point is excited by incident radiation. In the case of a line of such points with incident radiation normal to the line, the spherical wave fronts sent out by the line will reinforce and interfere so that a cylindrical wave front and several conical wave fronts will be formed just as an ordinary line grating gives first, second, and third order reflections of any wave length. The equally spaced line of radiating points, then, sends out rays in a series of cones and in a plane normal to the line (a degenerate cone corresponding to the cylindrical wave front). If the incident ray is not normal, the cylindrical wave front will not, in general, exist. Analytically, the phenomenon may be described so: if radiation strikes a line of diffracting points such that the cosine of the angle between the radiation and the line is α_0 , there will be reinforcement in all directions such that, if α is the cosine of the angle between any direction and the line of points,

$$h\lambda = a(\alpha - \alpha_0) \quad \text{where } h \text{ is an integer and } a \text{ is}$$

the distance between points in the line. When a series of such lines, parallel and equally spaced so that they form a two dimensional grating, is under the influence of radiation, cones of radiation are sent out from all the lines in all directions in the grating and these radiations reinforced and interfere with each other as did the radiations forming the spherical wave fronts. Reinforcement occurs where the cones of radiation intersect and interference is practically complete elsewhere if the grating is large, so that the only detectable diffracted radiation is

in a series of single rays instead of conical sheets. Analytically, there are two equations to be satisfied,

$$\begin{aligned} h\lambda &= a(\alpha - \alpha_0) \text{ and} \\ k\lambda &= b(\beta - \beta_0) \end{aligned}$$

for any two nonparallel lines of points. Diffraction from a three dimensional grating, made up of regularly spaced similar layers of points, will occur when rays from all the layers, or planes, coincide and reinforce each other. If this does not occur, interference will blot out the already weak radiation and there will be no diffraction observable. In this case there are three equations to be satisfied,

$$\begin{aligned} h\lambda &= a(\alpha - \alpha_0), \\ k\lambda &= b(\beta - \beta_0), \text{ and} \\ l\lambda &= c(\gamma - \gamma_0). \end{aligned}$$

and they will not, in general, be simultaneously satisfied unless something other than α , β , and γ is made variable. These are the Laue equations, named for their discoverer, M. v. Laue. Sir William H. Bragg has expressed the same facts by the equation,

$$n\lambda = 2d\sin\theta$$

This equation emphasizes the fact that every beam of diffracted radiation may be superficially regarded as a specular reflection from some plane of points in the crystal lattice. In that case, θ is half the angle between the incident and diffracted beams, and d is the smallest distance between parallel reflecting lattice planes. Ordinarily, then, it is necessary to introduce some variable in an experiment involving diffraction of X-rays by a three dimensional grating, and this may be done by using white X-radiation made up of a wide band of frequencies, or by rotating the lattice in a beam of monochromatic radiation. Both methods are used in crystal structure investigations.

In the first method, originally used by M. v. Laue, it is best to use a tube with a heavy metal target at high voltage to get the most efficient production of continuous Xradiation. In this laboratory, the source of continuous radiation is a permanently evacuated glass Coolidge tube with a tungsten target which is operated at about 56,000 volts. The minimum wave length is about 0.24\AA . The radiation used is confined to a narrow beam by use of two pinholes lined up with the source, and this beam is directed onto the crystal which is in front of a photographic film. The crystal is mounted with wax on a goniometer head with provision for precisely adjusting the position of the crystal by rotation or translation about or along three mutually perpendicular axes. The film is flat and perpendicular to the beam of Xrays.

For the other type of photograph made with monochromatic radiation and a moving crystal, this laboratory uses apparatus with molybdenum, iron, and copper targets and arrangements for oscillating a crystal about a given position or rotating it through 360° . The Xrays are produced in a tube of the ionization type. A glass tube is evacuated to a pressure of about .02 mm. of mercury and an aluminum cathode inside the tube is charged to about 40,000 volts. Air is ionized by the high voltage and positive particles strike the aluminum cathode and knock out electrons which shoot away from the cathode and strike the walls of the tube or the target. The aluminum at the end of the cathode is shaped so that the electrons shooting away from it are focussed either to a short line or a point (depending on the shape of the aluminum) on the copper, molybdenum, or iron target. These high energy electrons, in entering the atomic fields of the target, are quickly decelerated in one or more steps and emit Xrays with

frequencies depending on the energy lost by the electron in a single step. Some electrons knock out electrons from the inner shells of the atom, and, when other electrons in outer shells drop into the holes so formed, X-rays of frequency corresponding to the difference in energy level of the two shells are emitted. The X-rays emitted as a result of simple deceleration have frequencies covering a wide range and are called general radiation. X-rays emitted by electrons dropping from one shell to another have fixed frequencies which depend on the atom and the orbits involved, and are called characteristic radiation. The voltage of 40,000 is such that the intensity of the characteristic K_{α} radiation of the target is about a maximum with respect to the continuous radiation. Usually the background of continuous radiation is effectively removed by a filter, 40 μ of nickel in the case of copper radiation and 100 μ of zirconium in the case of molybdenum radiation. The filter strongly absorbs most of the radiation of higher energy than the characteristic frequency and at the same time lets through about one third of the characteristic radiation. The net effect of the filter is to cut down the intensity of the fogging continuous radiation more than the intensity of the useful monochromatic radiation.

The filtered X-rays are confined to a narrow beam by means of a series of pinholes or slits and the crystal placed in their path on a goniometer head which is in turn placed on a rotatable mount. The slit system is part of a stationary cylindrical camera which surrounds the crystal. An arrangement of motor and cams allows the mount to oscillate through angles of 5 $^{\circ}$, 10 $^{\circ}$, and 30 $^{\circ}$ and a gear arrangement provides for complete rotation.

There is also an apparatus which is similar to those described except that it uses a permanently evacuated hot cathode tube with a molybdenum target, and has arrangements allowing oscillation of the crystal through angles of $1\frac{1}{2}^{\circ}$, 6° , 12° , and 24° . The X-ray beam has about one tenth the intensity of that from the ionization tubes so that in this investigation it was used without a filter. The permanently evacuated tube, however, has two important advantages over the ionization tubes. It requires practically no attention and but one simple adjustment, and it is more constant in its behavior since there is no aluminum cathode to wear out.

The first X-ray photograph taken was a reflection from a natural rhombohedral face (110) using CuK_{α} radiation and oscillating through an angle of 30° . Measurements on this photograph were used, with the goniometrically determined angle α , to check Cox's results and to make sure that it was the same crystal he used.

MEASUREMENTS AND CALCULATIONS ON FIRST PHOTOGRAPH

Spot	Radius of camera = 5.00cm.			
	Dist. from cent. image	θ (rad.)	$\sin\theta$	$\sin(\theta+6\frac{1}{2}')$
1	1.266	.1266	.12620	.12812
2	2.573	.2573	.25446	.25628 = 2(.12814)
3	3.924	.3924	.38241	.38415 = 3(.12805)
mean $\frac{\sin\theta_i}{i} = .1281$				

The Bragg equation, $n\lambda = 2d\sin\theta$ solved for d/n gives

$$\frac{d}{n} = \frac{\lambda}{2\sin\theta} = \frac{1.5392}{2(.12812)} = 6.0079 = 6.01 \text{ \AA}$$

Using a previous value of α from less precise measurements of $73^{\circ} 55'$ and the equation,

$$\left(\frac{d}{n}\right)^2 = (h_1^2 + h_2^2 + h_3^2) b^2 + 2(h_1 h_2 + h_1 h_3 + h_2 h_3) b^2 \cos\beta$$



c.l.

Oscillation Photograph Reflecting $\text{CuK}\alpha$ from $(110)_{rh}$

where h_1, h_2, h_3 are the indices of the reflecting plane,

$$b = \frac{\sin \alpha}{a \sqrt{1 + 2 \cos^2 \alpha - 3 \cos^2 \alpha}} \quad \text{and} \quad \cos \beta = \frac{\cos^2 \alpha - \cos \alpha}{\sin^2 \alpha}$$

we get $\left(\frac{d}{n}\right)^{-2} = 2b^2(1 + \cos \beta) = 2b^2 \left(\frac{1 - \cos \alpha}{\sin^2 \alpha}\right) = \frac{2 \sin^2 \alpha}{a^2(1 + 2 \cos^2 \alpha - 3 \cos^2 \alpha) \sin^2 \alpha} \frac{(1 - \cos \alpha)}{\sin^2 \alpha} = \frac{2}{a^2(1 + \cos \alpha - 2 \cos^2 \alpha)}$

and $\frac{d}{n} = \frac{a}{\sqrt{2}} \sqrt{1 + \cos \alpha - 2 \cos^2 \alpha}$

so that $a = \frac{(6.0079)(1.4142)}{\sqrt{1 + 2.7704 - 2(1.27704)^2}} = 8.0157 \text{ \AA} \quad \text{if } n=1$

Using $\alpha = 74^\circ 14'$ we would get a larger value of a .

The next $\text{CuK}\alpha$ photograph used was a "complete rotation photograph" using a small crystal bathed in the X-ray beam and rotating the crystal at a constant speed about its vertical three-fold axis. Distances between the horizontal lines of spots, called layer lines, on the film were measured. From the smallest distance, the identity distance or lattice dimension in the direction of the three-fold axis was calculated by means of the Pölanyi equation, $h_i \lambda = a_i \sin \alpha$, wherein h is the number of a layer line counting from the equator as zero, α is the angle formed by the layer line, crystal, and equator, and a is the identity distance parallel to the axis about which the crystal is rotated. From measurements of equatorial reflections (reflections normal to the axis of rotation), the smallest identity distance normal to the three fold axis was calculated. It was assumed that there were no absences in the equator because all the reflections could be indexed on that basis, and because such indexing led to a value of α in agreement with the goniometric value. The two distances defined a hexagonal unit describing the lattice and from them the rhombohedral axis and angle were calculated. My measurements gave $a = 7.942 \text{ \AA}$ and $\alpha = 74^\circ 20'$. Measurements by Dr. Sturdivant of this laboratory gave 7.977 \AA and $73^\circ 59'$.

MEASUREMENTS ON 360° PHOTOGRAPH WITH CALCULATIONS

Layer lines		$\tan \alpha$	$\sin \alpha$
6	6.82	1-1	.0925
5	7.49		
4	8.09	2-2	.184
3	8.61		
2	9.09	3-3	.281
1	9.55		
0	10.00	4-4	.3855
-1	10.475		
-2	10.93	5-5	.505
-3	11.42		
-4	11.945	6-6	.639
-5	12.54		
-6	13.21		

$$\lambda_3 = \frac{\lambda h}{\sin \alpha} = \frac{1.5387}{.090117} = 17.0745 \text{ \AA}$$

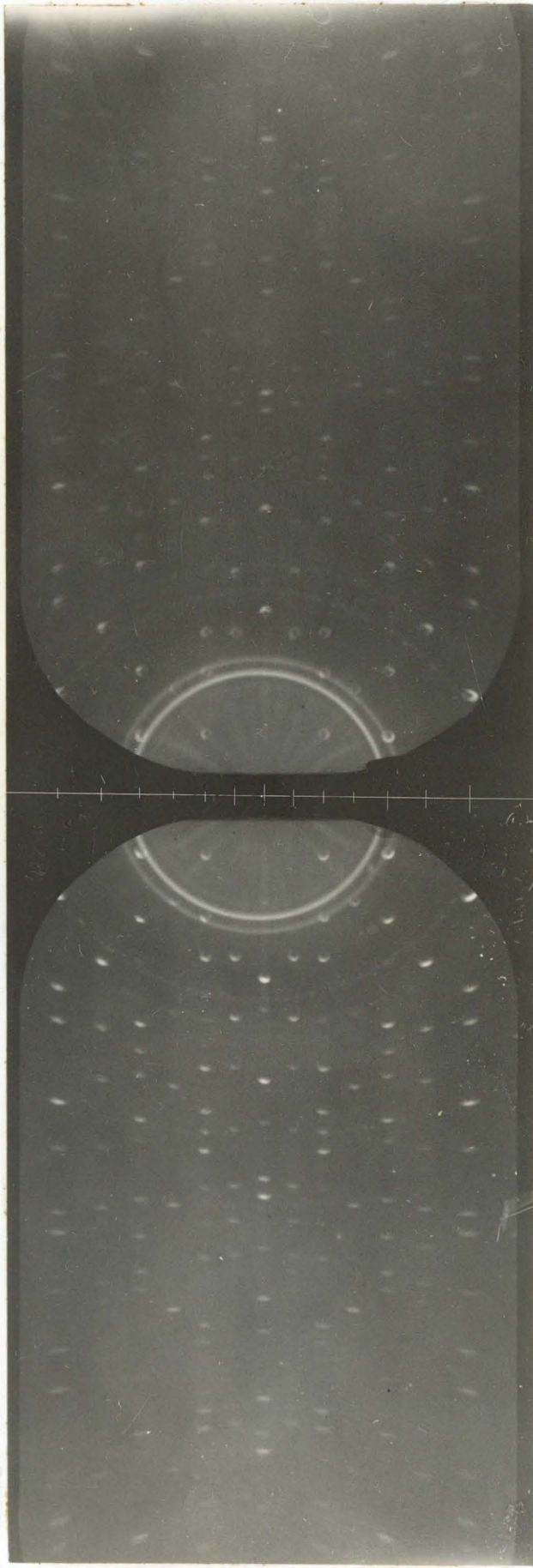
$$\text{mean } \frac{\sin \alpha}{h} = .090117$$

Equatorial measurements

Dist. from cent. image	θ	$\sin \theta$	$\sqrt{s/3}$	$\frac{\sin \theta}{\sqrt{s/3}}$	$(hkl)_{\text{hex}}$
16.25	9° 19'	.16177	1	.16177	(110)
28.2	16° 9'	.27824	1.732	.1606	(300)
32.8	18° 48'	.32216	2	.16108	(220)
43.8	25° 6'	.42415	2.646	.1604	(410)
50.3	28° 51'	.48244	3	.16081	(330)
58.7	33° 38'	.55386	3.464	.1598	(600)
61.5	35° 14'	.57693	3.606	.1600	(520)
69.5	39° 49'	.64040	4	.16010	(440)
77.1	44° 10'	.69681	4.359	.1599	(710)
82.0	47° 1'	.73155	4.583	.1596	(630)
92.5	53° 0'	.79864	5	.15973	(550)
97.9	56° 55'	.82993	5.196	.1597	(900)
100.7					
100.7	57° 42'	.84522	5.292	.1598	(820)
109.4	62° 41'	.88848	5.568	.1596	(740)

$$\text{Mean} = .1603$$

$$\lambda_1 = \frac{\lambda}{\sin \theta / \sqrt{s/3}} = \frac{1.5387}{.16036} = 9.595 \text{ \AA}$$

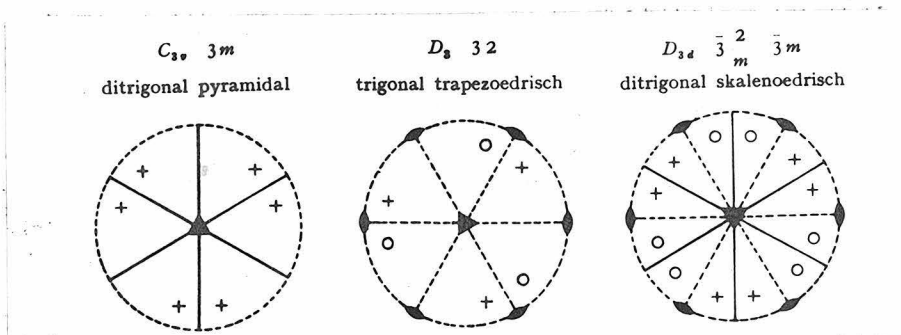


Complete Rotation Photograph with $CuK\alpha$

From these values of the hexagonal axes, the rhombohedral dimensions were calculated.

After the determination of a possible unit, the next step was its confirmation and a determination of the space group. This is best done by means of Laue photographs which use a small wave length X-ray and consequently show a large number of reflections. Laue photographs were taken with the beam of X-rays parallel to the three-fold axis. The photograph had symmetry D_{3d} showing a three-fold axis and three planes of symmetry. More photographs were taken with the three-fold axis at 4° and 8° to the beam of X-rays and the three photographs were indexed on the basis of a unit cell of the dimensions found previously. From the sine of the angle of reflection and the indices, the wave length of the radiation reflecting from each plane was calculated and, since no reflection out of several hundred seemed to come from a wave length below the lower limit of wave length in the beam, one can be fairly certain that the unit chosen is not too small. Because several of the wave lengths calculated to be quite close to the minimum wave length, the unit was assumed not to be too large. Calculation on the basis of the unit chosen and the density determination showed there were only two molecules per unit cell. If the unit chosen were too large, it might be a body centered unit containing two simple units with $\alpha > 100^\circ$. In that case, all reflections with the sum of the indices odd would be absent. They are not. The unit, then, is not too large.

Laue symmetry D_{3d} permits point groups D_{3d} , C_{3v} , and D_3 since each of these groups combined with a center of symmetry gives D_{3d} , and, because X-ray experiments are centrosymmetric, they cannot distinguish between these point groups. However,



Stereographic Projections of the Point Groups

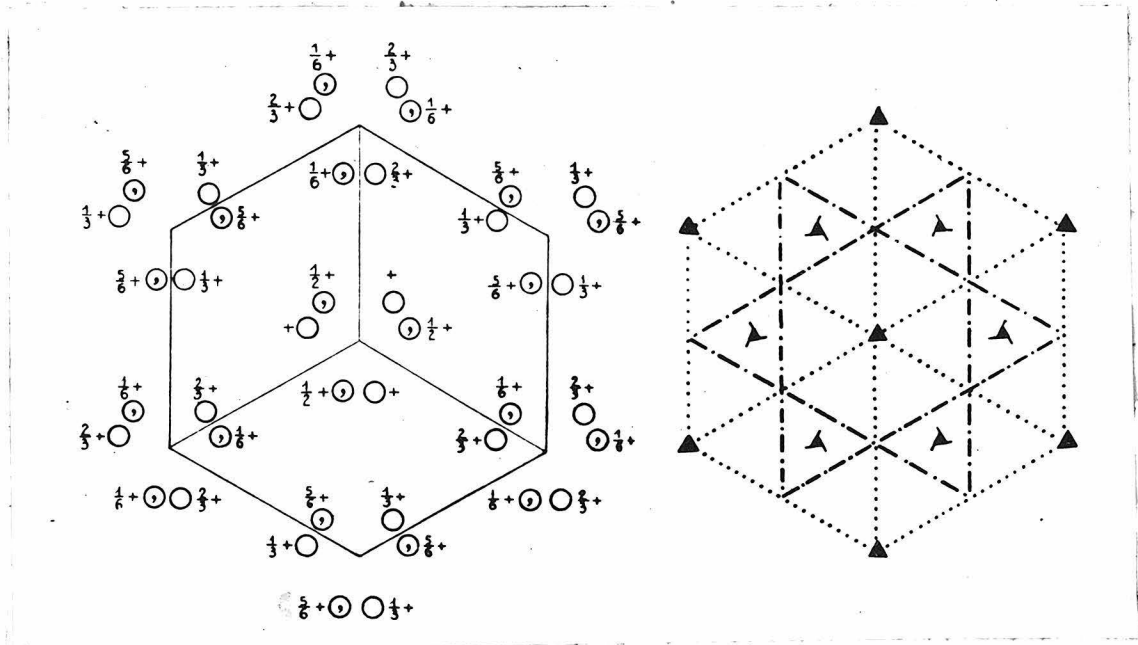
the crystals are pyroelectric and must, therefore, have a polar axis. D_{3d} has none, so the crystals had to be C_{3v} or D_3 . It was further observed in the pyroelectric experiment that the ends of three fold axis became charged and that that axis was, therefore, polar. The point group, then, can only be C_{3v} .

Fourteen reflections from different planes of the general form $\{hhl\}$ with l odd were not observed when they were in position to reflect. These were $(\bar{1}\bar{1}.11)$, $(\bar{1}\bar{1}9)$, $(\bar{1}\bar{1}7)$, $(\bar{1}\bar{1}5)$, $(\bar{2}\bar{2}7)$, $(\bar{2}\bar{2}5)$, $(22\bar{3})$, $(33\bar{5})$, $(44\bar{3})$, $(44\bar{5})$, $(44\bar{7})$, $(55\bar{7})$, $(66\bar{5})$, and $(77\bar{1})$. No first order reflections of this form were observed. C_{3v}^6 is the only space group which requires these absences so it would seem that that is the space group. C_{3v}^6 is also the only C_{3v} space group that requires two molecules per unit cell.

When KCN and CuCN are mixed to form the potassium cuprocyanide, heat is evolved and the resulting salt is colorless. Addition of ammonia does not produce a blue color and addition of ferricyanide does not give a red precipitate. Addition of ferricyanide and acid does, however, ~~does~~ give a red precipitate. It would seem

from this evidence that the copper is strongly bound. However, there was always a smell of cyanide from the crystallizing solutions which may mean that the tetracyano complex is not extremely stable. Four cyanides are presumably bound to one copper and, since there is a threefold axis in a unit cell with only two copper molecules, the cyanides must be arranged in some form with a trigonal axis. It is assumed on the basis of work of Cox, Wardlaw, and Webster and of valence bond considerations that the arrangement is tetrahedral. Since the chosen space group has a glide plane parallel to the three fold axis, the two tetracyanide tetrahedra are arranged with ^{one cyanide} parallel to and coincident with the trigonal axis and pointing in the same direction, and the other three at θ , $\theta+120^\circ$, and $\theta+240^\circ$ to a plane containing the trigonal axis and a rhombohedral axis in one case and $-\theta$, $-(\theta+120^\circ)$, $-(\theta+240^\circ)$ in the other case. The Cu-C and C \equiv N bond distances can be estimated fairly accurately from known atomic radii and bond lengths determined in previous work.

The Cu⁺ tetrahedral covalent radius was taken as 1.35\AA^4 and the C single bond radius taken as $.77\text{\AA}^4$ so that the Cu-C distance becomes 2.12\AA . The C \equiv N triple distance of 1.15\AA^5 was used. No simple method was found for fixing the position of the potassiums in any way. There are, then, four variables or parameters which must be determined to fix the structure completely. They are θ for the cyanide tetrahedra and three for the K⁺. These three may be listed as θ_k (angle between the plane of the rhombohedral axis and the radius from the three-fold axis to the K⁺), r_k (the length of the radius), and z_k (the distance parallel to the three-fold axis between a copper atom and a K⁺).



$C_{3v}^6 - R3c$.

Rhomboedr. Beschreibung.

Punktlagen:

- 2: (a) xxx ; $\frac{1}{2} + x, \frac{1}{2} + x, \frac{1}{2} + x$.
 6: (b) xyz ; zxy, yzx ;
 $\frac{1}{2} + y, \frac{1}{2} + x, \frac{1}{2} + z$; $\frac{1}{2} + z, \frac{1}{2} + y, \frac{1}{2} + x$;
 $\frac{1}{2} + x, \frac{1}{2} + z, \frac{1}{2} + y$.

Punktsymmetrie:

- $C_3 - 3$ in (a).
 $C_1 - 1$ in (b).

Hexagonale Beschreibung:

Punktlagen: $(000; \frac{1}{3}\frac{2}{3}\frac{2}{3}; \frac{2}{3}\frac{1}{3}\frac{2}{3}) +$

- 6: (a) $00z$; $0, 0, \frac{1}{2} + z$.
 18: (b) xyz ; $\bar{y}, x - y, z$; $y - x, \bar{x}, z$;
 $y, \bar{x}, \frac{1}{2} + z$; $x, x - y, \frac{1}{2} + z$;
 $y - x, y, \frac{1}{2} + z$.

Gitterkomplexe:

- $D_{3d}^5 - R\bar{3}m$ (a) in (a).
 $C_{3v}^6 - R3c$ (b) in (b).

Auslöschungen: Rhomboedrische Beschreibung:

Allgemein: (hkl) in allen Ordnungen vorhanden; (hhl) nur mit $l = 2n$ vorhanden.

Speziell: Für die spezielle Punktlage (a) bestehen die weiteren Auslöschungen: (hkl) nur mit $h + k + l = 2n$ vorhanden.

Hexagonale Beschreibung:

Allgemein: (hki) nur mit $h - k + l = 3n$ vorhanden; $(h, h, 2h, l)$ nur mit $l = 3n$ vorhanden, $(h\bar{h}0l)$ nur mit $2h + l = 3n$ und $l = 2n$ vorhanden.

Speziell: Für die spezielle Punktlage (a) gelten die weiteren Auslöschungen: (hki) nur mit $h - k + l = 3n$ und $l = 2n$ vorhanden.

If we consider the hexagonal unit of $K_3Cu(CN)_4$ containing six molecules, it is evident that, if the cyanide tetrahedra are assumed to be regular, the positions of all the atoms except K^+ are fixed in the z direction or direction of the three-fold axis. Reflections from planes normal to the three-fold axis are dependent only on the location of atoms along the three-fold axis and not on their distribution in a plane normal to that axis. Consideration of the structure factor of C_{3v}^6 , hexagonal unit, shows this analytically and suggests a way of fixing the z_k parameter independently of the other parameters.

The general form of the structure factor is⁶

<p>— Hexagonal indices.</p> <p>$000, \frac{1}{3}\frac{2}{3}\frac{1}{3}, \frac{2}{3}\frac{1}{3}\frac{2}{3} + xy\bar{z}; \bar{y}, x-y, z; y-x, \bar{x}, \bar{z}; \bar{y}, \bar{x}, \frac{1}{2}+z; x, x-y, \frac{1}{2}+z; y-x, y, \frac{1}{2}+z$</p>	
$A = 2\left(1 + 2\cos 2\pi\frac{h-k+l}{3}\right) \left\{ \cos \pi \left[(h-k)(x-y) + 2lz + \frac{l}{2} \right] \cos \pi \left[i(x+y) + \frac{l}{2} \right] + \right.$ $\quad \left. + \cos \pi \left[(k-i)(x-y) + 2lz + \frac{l}{2} \right] \cos \pi \left[h(x+y) + \frac{l}{2} \right] + \right.$ $\quad \left. + \cos \pi \left[(i-h)(x-y) + 2lz + \frac{l}{2} \right] \cos \pi \left[k(x+y) + \frac{l}{2} \right] \right\}$	
$B = 2\left(1 + 2\cos 2\pi\frac{h-k+l}{3}\right) \left\{ \sin \pi \left[(h-k)(x-y) + 2lz + \frac{l}{2} \right] \cos \pi \left[i(x+y) + \frac{l}{2} \right] + \right.$ $\quad \left. + \sin \pi \left[(k-i)(x-y) + 2lz + \frac{l}{2} \right] \cos \pi \left[h(x+y) + \frac{l}{2} \right] + \right.$ $\quad \left. + \sin \pi \left[(i-h)(x-y) + 2lz + \frac{l}{2} \right] \cos \pi \left[k(x+y) + \frac{l}{2} \right] \right\}$	
$\begin{cases} h-k+l = 3n \\ l = 2n \end{cases}$	$A = 6 \left\{ \cos \pi \left[(h-k)(x-y) + 2lz \right] \cos \pi i(x+y) + \cos \pi \left[(k-i)(x-y) + 2lz \right] \times \right.$ $\quad \left. \times \cos \pi h(x+y) + \cos \pi \left[(i-h)(x-y) + 2lz \right] \cos \pi k(x+y) \right\}$ $B = 6 \left\{ \sin \pi \left[(h-k)(x-y) + 2lz \right] \cos \pi i(x+y) + \sin \pi \left[(k-i)(x-y) + 2lz \right] \times \right.$ $\quad \left. \times \cos \pi h(x+y) + \sin \pi \left[(i-h)(x-y) + 2lz \right] \cos \pi k(x+y) \right\}$ $B = 0 \text{ if } h=k \text{ and } l=0 \text{ (etc. etc.)}$

For planes of the type (00.l), this reduces to

$$A = 18 \cos 2\pi lz \quad B = 18 \sin 2\pi lz$$

and F^2 , which is proportional to the corrected intensity,

$$= (\sum A)^2 + (\sum B)^2$$

z is the z parameter of each atom in the cell. The z are fixed for every atom but the K^+ so it is possible to plot the structure

factor, F^2 , against all possible values of z_k .

The z parameters were calculated for Cu, C, and N on the basis of the assumed bond angles and distances and their contribution to the structure factor worked out. Contributions to the structure factor of the potassium for each of several z_k were worked out and tabulated. These values were added to the rest of the structure factors and the results plotted against the z_k parameter. Scattering factors for Cu, C, and N were obtained from a paper of Pauling and Sherman⁷ and for K^+ from the International Crystal Structure Tables⁸.

Photographs were then taken of reflections from planes of the form $(00.l)_{\text{hex}}$ using a large, ground $(00.l)$ face. Because only planes of the form $(00.6n)$ had structure factors not zero, only three such planes could be photographed with CuK_α radiation. Intensity measurements were made but were not used in the final evaluation of the potassium z parameter. Use of MoK_α radiation made it possible to get reflections from eight planes up to (00.48) , but only five were photographed because the reflections from (00.24) and (00.30) were already extremely weak and because five reflections were enough to determine the parameter with fair accuracy.

The intensity estimating scale or wedge was made by photographing a slit image on a strip of film with varying time of exposure. The slit was cut to the approximate shape of the reflections as observed on the film and placed far enough from the film during the exposures to give the right degree of fuzziness. Intensities were estimated by superimposing the film and wedge and comparing the spots by transmitted light. All the spots in the final measurements were made at the same time under the

same conditions except as to the amount of fog on the film and they all were of about the same intensity. Since the wedge and film, in the comparison, had the same fog for background, the chance for error on that account is small. Estimates of intensity were reproducible to within ten percent and the error in estimation of relative intensity was probably not greater than ten percent. The exposures were probably measured to within three percent, but variations in the voltage may have increased this error to fifteen percent, probably to less than ten percent. Two types of film were use, but the relative sensitivity had been measured and is probably good to one percent⁸. The Lorentz and polarization factors were obtained by interpolation from the crystal structure tables⁹.

INTENSITY COMPARISON ON FINAL MoK_α (00.1) PHOTOS

Plane reflecting	Intensity	Lorentz & Polar. Fact.	Temp. Factor	F ² × Const.
(00.6)	2.24	7.973	.961	2.93
(00.12)	.790	3.746	.866	2.437
(00.18)	.423	2.295	.680	2.710
(00.24)	.0758	1.486	.506	1.007
(00.30)	.0181	1.096	.401	0.4115

In the crystal structure tables, there is a list of crystals and their critical temperatures. A critical temperature was chosen to correspond to the hardness of the crystal and and the temperature factor calculated with the help of the tables¹⁰. The critical temperature chosen was 280°K. and, from it, B, in the formula for the temperature factor, $\left[e^{-B \left(\frac{\sin \theta}{\lambda} \right)^2} \right]^2$ was calculated to be 0.595 Å².

CALCULATION OF CONTRIBUTION TO STRUCTURE FACTORS OF $(00.l)_h$
OF ATOMS OTHER THAN POTASSIUM

$(00.6)_h$ hex

Atom	lz	$\cos 2\pi lz$	f	$f \cos 2\pi lz$	$\sin 2\pi lz$	$f \sin 2\pi lz$
Cu	0.0	1	24.89	24.89	0	0
C	.736	-.0879	4.04	-.3551	-.9961	-4.024
3C	.755	.0314	12.12	.3807	-.9995	-12.114
N	.135	.6613	5.33	3.524	.7501	4.000
3N	.622	-.7203	15.99	-11.515	-.6937	-11.09
				<u>16.9246</u>		<u>-23.228</u>

$(00.12)_h$ hex

Atom	lz	$\cos 2\pi lz$	f	$f \cos 2\pi lz$	$\sin 2\pi lz$	$f \sin 2\pi lz$
Cu	0.0	1	18.19	18.19	0	0
C	.472	-.9846	2.11	-2.078	.1750	0.3692
3C	.510	-.9980	6.33	-5.818	-.0628	-0.3976
N	.270	-.1253	2.77	-0.347	.9921	2.748
3N	.244	.0377	8.31	0.313	.9993	8.304
				<u>10.260</u>		<u>11.0236</u>

$(00.18)_h$ hex

Atom	lz	$\cos 2\pi lz$	f	$f \cos 2\pi lz$	$\sin 2\pi lz$	$f \sin 2\pi lz$
Cu	0.0	1	12.27	12.27	0	0
C	.208	.2608	1.64	.4277	.9654	1.583
3C	.265	-.0941	4.92	-.463	.9956	4.918
N	.405	-.3281	1.84	-.6020	.5621	1.035
3N	.866	.6660	5.52	3.677	-.7459	-4.118
				<u>15.3097</u>		<u>3.418</u>

$(00.24)_h$ hex

Atom	lz	$\cos 2\pi lz$	f	$f \cos 2\pi lz$	$\sin 2\pi lz$	$f \sin 2\pi lz$
Cu	0.0	1	8.04	8.04	0	0
C	.944	.9387	1.51	1.417 ⁵	-.3446	-.5201
3C	.020	.9921	4.53	4.493	.1253	.5678
N	.540	-.9686	1.56	-1.511	-.2487	-.3880
3NN	.488	-.9972	4.68	-4.666	.0753	.3524
				<u>7.7735</u>		<u>-.0121</u>

$(00.30)_h$ hex

Atom	lz	$\cos 2\pi lz$	f	$f \cos 2\pi lz$	$\sin 2\pi lz$	$f \sin 2\pi lz$
Cu	0.0	1	7.59	7.59	0	0
C	.680	-.4258	1.35	-.5746	-.9048	-1.2215
3C	.775	.1564	4.05	.5834	-.9877	-4.000
N	.675	-.4540	1.45	-.654	-.8911	-1.292
3N	.110	.7705	4.35	3.353	.6374	2.772
				<u>10.2978</u>		<u>-3.7415</u>

STRUCTURE FACTORS OF $(00.l)_h$ PLANES FOR VARIOUS z_k VALUES

$(00.6)_h$ hex

lz_k	$f_k \cos 2\pi lz$	$f_k \sin 2\pi lz$	$(\sum f_i \cos 2\pi lz_i)^2$	$(\sum f_i \sin 2\pi lz_i)^2$	F^2
1.0	14.13	0	964.4	539.4	1504.
.90	11.43	- 8.30	804.0	996.0	1800.
.81	5.20	-13.14	489.7	1323.	1803.
.72	-2.65	-13.88	203.8	1379.	1583.
.63	- 9.68	-10.30	52.6	1126.	1179.
.54	-13.68	- 3.52	10.5	716.5	727.0
.45	-13.44	4.36	12.1	356.5	368.6
.36	- 9.00	10.89	62.8	152.6	215.4
.27	- 1.77	14.02	229.5	85.2	314.7
.18	6.02	12.79	526.3	109.2	635.5
.09	11.93	7.56	833.0	245.1	1078.

$(00.12)_h$ hex

2.0	9.78	0	400.2	121.3	521.5
.80	3.02	- 9.30	176.3	413.1	589.4
.62	- 7.13	- 6.70	9.8	314.1	323.9
.44	- 9.10	3.60	1.4	55.1	56.5
.26	- 0.61	9.76	93.1	1.6	94.7
.08	8.57	4.71	354.5	39.8	394.3
.90	7.92	- 5.75	330.1	281.4	611.5
.72	- 1.83	- 9.60	71.1	425.7	496.8
.54	- 9.47	- 2.43	0.6	181.0	181.6
.36	- 6.23	7.54	16.2	12.2	28.4
.18					

$(00.18)_h$ hex

3.0	7.98	0	542.0	11.7	553.7
.70	- 2.47	- 7.59	164.9	17.4	192.3
.43	- 7.22	3.40	65.5	46.5	112.0
.16	4.23	6.74	353.9	103.3	457.2
.89	6.15	- 5.08	460.0	2.8	462.8
.62	- 5.74	- 5.46	91.6	4.2	95.8
.08	7.00	3.84	497.8	52.8	550.6

$(00.24)_h$ hex

z_k					
.000	7.18	0	223.6	0.0	223.6
.0075	3.11	6.50	118.5	42.4	160.9
.015	- 4.58	5.53	11.5	30.8	42.4
.0225	- 6.96	- 1.79	0.7	3.1	3.8
.030	- 1.35	- 7.05	41.4	49.6	91.0
.0375	5.81	- 4.22	184.3	17.7	202.0
.045	6.39	- 3.46	200.7	11.9	212.6

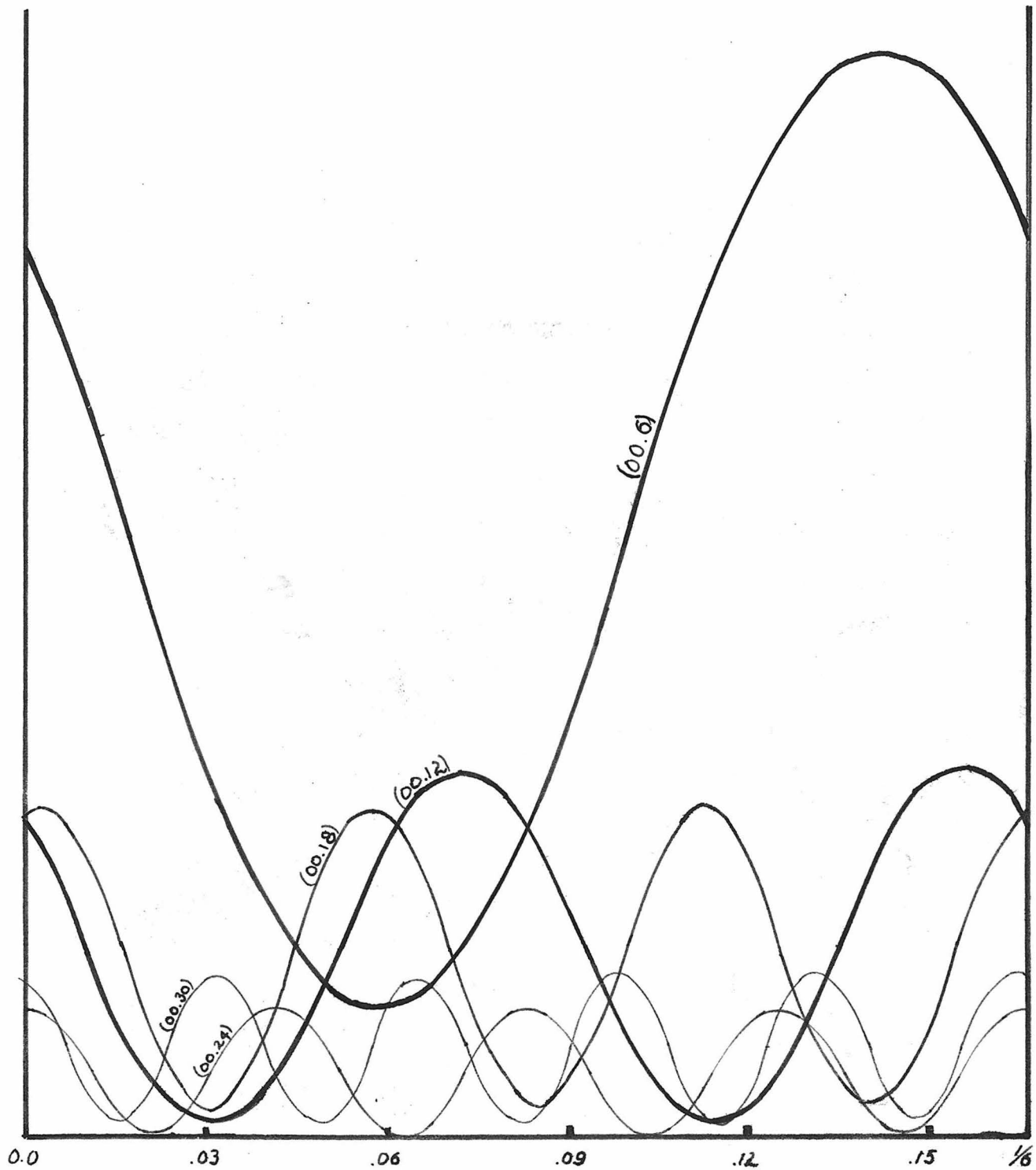
Final F^2 values corrected for the temperature effect were compared with the plot of F^2 against z_k and one spot found where a qualitative fit could be made. Various values of B were now assumed and new ratios of F^2 calculated in an attempt to get a perfect fit. The best fit, with a variation from the plot of only $\pm 6\%$, was obtained for $B=1.45$, corresponding to a critical temperature of about 130°K . Since, however, the total error in intensity ratios may have amounted to over 60%, this calculation cannot be regarded as significant except in that it shows that the temperature factor is not of very great importance in fixing parameters. The z_k parameter turned out to be $1.042 - .046 + n/6$.

F^2 RATIOS FOR VARIOUS TEMPERATURE FACTORS

B = 0	B = .595	B = 1.0	B = 1.4	B = 1.5	B = 2.0
2.81	2.93	3.00	3.07	3.09	3.20
2.11	2.44	2.70	2.97	3.04	3.46
1.84	2.71	3.17	3.94	4.17	5.46
0.51	1.01	1.34	1.98	2.18	3.52
0.17	0.41	0.74	1.35	1.57	3.32

The critical temperature for $B=2.0$ is about 90°K .

Probably the greatest source of error in the determination of the intensities was caused by the deteriorating surface of the crystal. From the time of grinding the crystal face to the time of taking the final photographs, crystal growths formed on the ground face and were wiped off three or four times. It would probably be advisable before starting the determination of the other three parameters to regrind the crystal face or grind a new face



$Z_{K^+} \longrightarrow$

Structure Factors of $K_3Cu(CN)_4$ for Various Z_{K^+}

and take new photographs for more accurate intensity measurements and a more accurate parameter determination.

Summary

Crystals of potassium cuprocyanide were prepared and analyzed. The analysis showed them to be $K_3Cu(CN)_4$. The hardness was found to be 2.4; the density was found to be 1.99 ± 0.1 . The crystals were found, by a pyroelectric experiment, to have a polar three-fold axis.

The crystal habit and unit cell reported by Cox, Wardlaw, and Webster were confirmed and the space group found, by examination of Laue photographs, to be C_{3v}^6 .

It was assumed that the tetracyanide complex formed a regular tetrahedron, and, by intensity measurements made on five $(00.l)_{hex}$ reflections, the hexagonal z parameter of the potassium ion was found to be $.042 - .046 + n/6$.

REFERENCES

1. Cox, Wardlaw, and Webster, J. C. S. 1936 p. 775
2. Bassett and Corbet, J. C. S. 125 p. 1667 (1924)
3. Chemical Rubber Co. Handbook, 17th Ed. p. 964
4. Internationale Tabellen zur Bestimmung von Kristallstrukturen,
p. 625
5. Pauling and Brockway, J. A. C. S. 59 p. 1223 (1937)
6. Lonsdale, Structure Factor Tables
7. Pauling and Sherman, Z. Krist. 81 p. 1 (1932)
8. Gamertsfelder and Gingrich, Rev. Sci. Instr. 9 p. 154 (1938)
9. Int. Tab. z. Best. v. Krist., p. 567
10. Ibid., p. 574