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The Application of the Anomalous Scattering of X-rays to the Solution of the Crystal Structure of $(NH_4)_2VO(NCS)_4.5H_2O$

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A method is described for the use of the anomalous scattering of X-rays in the solution of the phase problem for the centrosymmetric case. It requires comparison of structure amplitudes measured with two different X-radiations. The practical application of this method to the solution of the $(h0l)$ projection of diammonium oxotetrakis(isothiocyanato)vanadate pentahydrate is described in some detail.

Introduction

When an atom scatters X-rays of wavelength (λ) close to its own K absorption edge (λ_K) the usual atomic scattering factor f_0 must be replaced by $f=f_0+\Delta f'+i\Delta f''$, where $\Delta f'$ and $\Delta f''$ are the real and imaginary parts of the anomalous dispersion correction (James, 1954). This effect has been used by Bijvoet, Peerdeman & van Bommel (1951) to determine absolute configuration, and by Pepinsky & Okaya (1956) to assist in the solution of Patterson functions. In this paper an alternative procedure is discussed for the use of anomalous scattering in the solution of centrosymmetric structures in cases where $\lambda/\lambda_K>1$.† The practical application of this method to the solution of the structure of diammonium oxotetrakis(isothiocyanato)vanadate pentahydrate is described, this being a structure which had proved insoluble by other methods.

Theory

The following assumptions are made:

(i) Only one type of atom scatters anomalously with the exciting radiation, and all atoms scatter normally with a second radiation.

(ii) The imaginary part of the scattering factor may be neglected, and the atomic scattering factor becomes $f=f_0+\Delta f'$.

For $\lambda\simeq\lambda_K$ and $\lambda/\lambda_K>1$, the values of $|\Delta f''|$ are 10–20% that of $|\Delta f'|$; Hönl's formula (James, 1954) gives $\Delta f''=0$ for these cases.

For the centrosymmetric case the expression for the structure factors then becomes:

$$F_a(\mathbf{H})=\sum_a (f_a+\Delta f'_a)\cos 2\pi\mathbf{H}.\Theta_a+\sum_n f_n\cos 2\pi\mathbf{H}.\Theta_n \quad (1)$$

where $F_a(\mathbf{H})$ is the structure factor when anomalous scattering occurs; $\mathbf{H}=(h,k,l)$; $\Theta_i=(x_i,y_i,z_i)$ for an atom i, the subscripts a referring to atoms which scatter anomalously, and n to the other atoms; f now refers to the usual value of the scattering factor. For normal scattering the structure factor $F(\mathbf{H})$ is given by:

$$F(\mathbf{H})=\sum_a f_a\cos 2\pi\mathbf{H}.\Theta_a+\sum_n f_n\cos 2\pi\mathbf{H}.\Theta_n\,. \quad (2)$$

Except for some very small structure factors

$$(|F|\le|\sum_a \Delta f'_a\cos 2\pi\mathbf{H}.\Theta_a|)\,,$$

where the smallness arises from the cancellation of the contributions from the normal and anomalous atoms, $F(\mathbf{H})$ and $F_a(\mathbf{H})$ will have the same sign, and so

$$\begin{aligned}||F(\mathbf{H})|-|F_a(\mathbf{H})|| &= |F(\mathbf{H})-F_a(\mathbf{H})|\\ &= |\sum_a(-\Delta f')\cos 2\pi\mathbf{H}.\Theta_a|\,, \end{aligned}\quad (3)$$

which is the modulus of the structure factor contribution from the K electrons of the anomalous scatterers. A Patterson function calculated with $(|F(\mathbf{H})|-|F_a(\mathbf{H})|)^2$ will contain only the vectors between the anomalous scatterers; these will usually be few, so that the Patterson function can be solved to give the positions of the anomalous scatterers. A similar use of the $(|F(\mathbf{H})|-|F_a(\mathbf{H})|)^2$ synthesis is described by Ramaseshan, Venkatesan & Mani (1957) in their structure determination of $KMnO_4$. There is now sufficient information available for the structure to be solved by the method of isomorphous replacement (Lipson & Cochran, 1953) for, combining (1) and (2) and noting that

$$\sum_a f_a\cos 2\pi\mathbf{H}.\Theta_a=f_a\sum_a\cos 2\pi\mathbf{H}.\Theta_a\,,$$

then

$$\frac{F(\mathbf{H})}{\sum_a\cos 2\pi\mathbf{H}.\Theta_a}=\frac{F_a(\mathbf{H})}{\sum_a\cos 2\pi\mathbf{H}.\Theta_a}-\Delta f'_a\,. \quad (4)$$

There are then three possible cases:

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† A procedure for the case where $\Delta f'\simeq\Delta f''$, *i.e.* $\lambda/\lambda_K<1$, will be described in a later paper when the method has been used, successfully or unsuccessfully, in a real crystal structure analysis.

(1) $F(\mathbf{H})$ and $\sum_a \cos 2\pi\mathbf{H}.\Theta_a$ have the same sign; then

$$\frac{|F(\mathbf{H})|}{|\sum_a \cos 2\pi\mathbf{H}.\Theta_a|}=\frac{|F_a(\mathbf{H})|}{|\sum_a \cos 2\pi\mathbf{H}.\Theta_a|}-\Delta f_a' \qquad (5)$$

and as $\Delta f_a'$ is negative, $|F(\mathbf{H})|>|F_a(\mathbf{H})|$.

(2) $F(\mathbf{H})$ and $\sum_a \cos 2\pi\mathbf{H}.\Theta_a$ have opposite signs; then

$$\frac{-|F(\mathbf{H})|}{|\sum_a \cos 2\pi\mathbf{H}.\Theta_a|}=\frac{-|F_a(\mathbf{H})|}{|\sum_a \cos 2\pi\mathbf{H}.\Theta_a|}-\Delta f_a' \qquad (6)$$

and $|F(\mathbf{H})|<|F_a(\mathbf{H})|$.

(3) $\sum_a \cos 2\pi\mathbf{H}.\Theta_a=0$ when $|F(\mathbf{H})|=|F_a(\mathbf{H})|$. (7)

As the coordinates of the anomalous scatterers are known the signs of $\sum_a \cos 2\pi\mathbf{H}.\Theta_a$ are known, and so comparison of $|F(\mathbf{H})|$ with $|F_a(\mathbf{H})|$ gives the signs of all the reflexions to which these atoms contribute and the structure can then be solved by Fourier methods. As with the Patterson function, errors may be introduced by structure factors which change sign when anomalous scattering occurs; since these structure factors are very small the errors introduced into the Fourier synthesis will be small.

Scaling of data

In the procedure described above, it has been assumed that the two sets of data have been placed on the correct absolute scale. Approximate scale factors may be obtained from Wilson's (1949) method; these should be sufficiently accurate for the $(|F(\mathbf{H})|-|F_a(\mathbf{H})|)^2$ synthesis. Once the positions of the anomalous scatterers have been determined, more accurate scale factors can be determining by plotting

$$\frac{|F_a'(\mathbf{H})|}{|\sum_a \cos 2\pi\mathbf{H}.\Theta_a|} \text{ against } \frac{|F'(\mathbf{H})|}{|\sum_a \cos 2\pi\mathbf{H}.\Theta_a|},$$

where $F_a(\mathbf{H})$ and $F'(\mathbf{H})$ are the structure factors on arbitrary scales; values are plotted in the top right hand quadrant (*C–D* in Fig. 1) or the bottom left hand quadrant (*A–B*) depending on whether the sign of the structure factor is the same as or opposite to the sign of $\sum_a \cos 2\pi\mathbf{H}.\Theta_a$. The relative scale factor may be determined from the gradient, and if the value of $\Delta f_a'$ is known the absolute scale factor may be determined*.

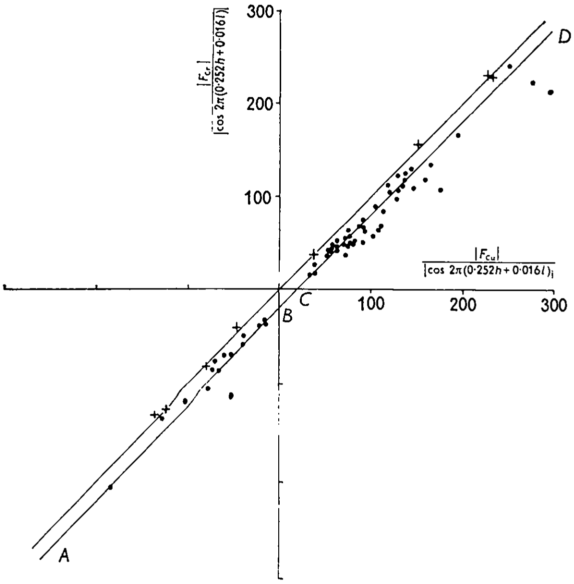

Fig. 1. Plot of $|F_{\text{Cr}}|/|\cos 2\pi(0{\cdot}252h+0{\cdot}016l)|$ against $|F_{\text{Cu}}|/|\cos 2\pi(0{\cdot}252h+0{\cdot}016l)|$.

The crosses represent structure amplitudes whose signs were either indeterminate or incorrectly determined.

Practical application to the structure of $(NH_4)_2VO(NCS)_4.5H_2O$

Diammonium oxotetrakis(isothiocyanato)vanadate pentahydrate, $(NH_4)_2VO(NCS)_4.5H_2O$, is monoclinic with space group $P2_1/n(C_{2h}^5)$ and unit-cell dimensions

$$a=16{\cdot}50\pm0{\cdot}05,\ b=6{\cdot}82\pm0{\cdot}02,\ c=16{\cdot}32\pm0{\cdot}05\ \text{Å};\ \beta=94{\cdot}5\pm0{\cdot}5^\circ;$$

there are 4 formula units in the cell.

A three-dimensional sharpened Patterson function gave the position of the vanadium atom as $\frac{1}{4}, \frac{1}{4}, 0$; a Fourier synthesis based on signs calculated from this vanadium position could not be interpreted. The vanadium atom contributes only to reflexions with h, k, l all even or all odd, giving false symmetry to electron density maps calculated from these reflexions (as in the $h0l$ projection, Fig. 2*a*); also, as was later shown, there are several reflexions with signs opposite to those of the vanadium contributions which gave rise to false peaks on the Fourier maps (Fig. 2*a* and *b*). There were insufficient large unitary structure factors for the successful use of structure factor graphs or sign relationships.

Since the wavelength of Cr $K\alpha$ radiation (2·291 Å) is close to the K absorption edge of vanadium (2·269 Å) it was possible to apply the method outlined above, by comparing intensities observed with Cu $K\alpha$ and Cr $K\alpha$ radiations.

Experimental

Intensity data for the $h0l$ projection were obtained from Weissenberg photographs by the multiple-film technique; the intensities were estimated visually by

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* Since this work was completed a similar method has been published by Caticha-Ellis (1962).

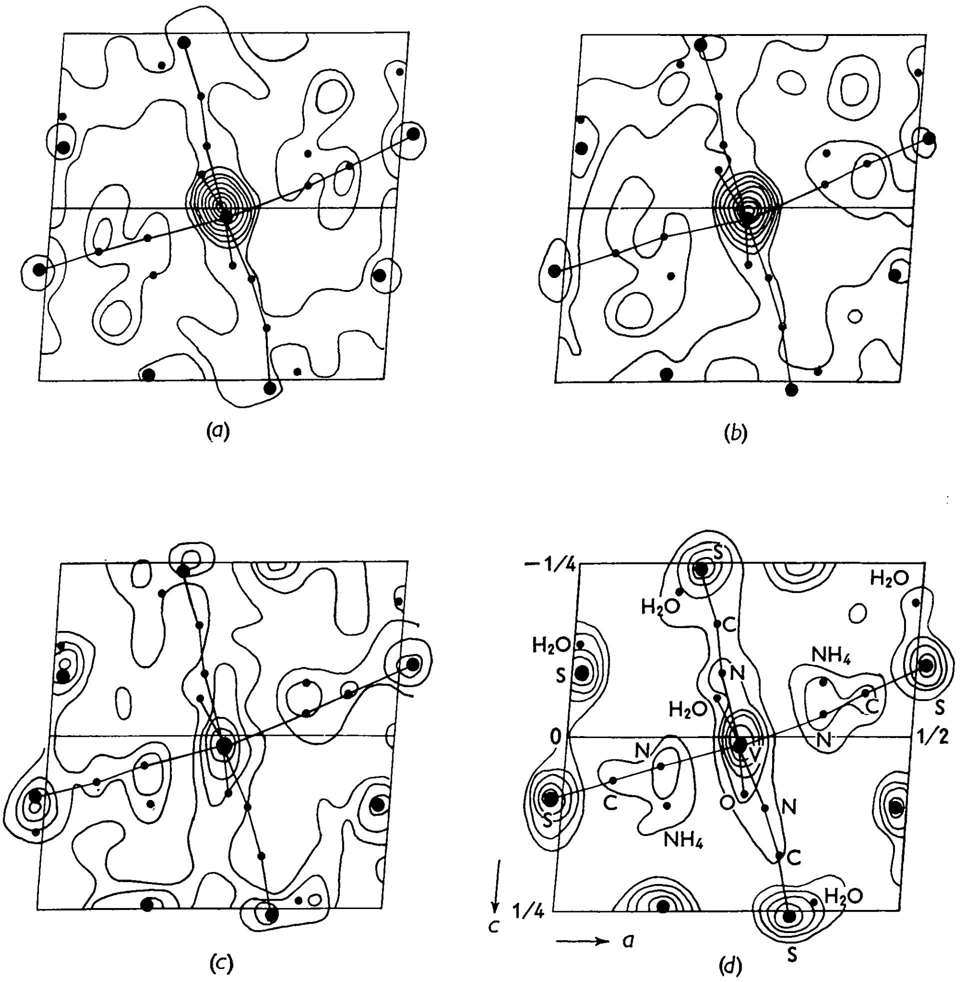

Fig. 2. $h0l$ electron density maps calculated with (a) Signs from vanadium at $x = 0{\cdot}250$, $z = 0{\cdot}000$, (b) Signs from vanadium at $x = 0{\cdot}252$, $z = 0{\cdot}016$, (c) Signs from anomalous scattering, (d) Signs from final three-dimensional refinement. The positions shown for the atoms are those determined from the final three-dimensional refinement.

means of a calibration strip. The same crystal, which was roughly cylindrical with mean radius 0·11 mm ($\mu r = 1{\cdot}0$ for Cu $K\alpha$ and $\mu r = 1{\cdot}8$ for Cr $K\alpha$) was used for both sets of observations. Approximate scale and temperature factors were obtained by Wilson's (1949) method, the observed structure factors were corrected for thermal motion and absorption, the values of the absorption correction used were those from *International Tables for X-Ray Crystallography* (1959). A more accurate value for the relative scale factor was later obtained by plotting $|F_{\mathrm{Cr}}|/|\cos 2\pi\mathbf{H}.\Theta_V|$ against $|F_{\mathrm{Cu}}|/|\cos 2\pi\mathbf{H}.\Theta_V|$ (Fig. 1).

Solution of the *h0l* projection

The anomalous dispersion corrections for all but the vanadium atom could be neglected (Table 1) and so the fundamental assumption (i) is justified and equation (4) in this example is:

$$F_{\mathrm{Cu}}/\cos 2\pi\mathbf{H}.\Theta_v = F_{\mathrm{Cr}}/\cos 2\pi\mathbf{H}.\Theta_v - \Delta f'_v$$

Table 1. *Anomalous dispersion corrections*

The values for vanadium are those of Dauben & Templeton (1955) and those for the other atoms calculated from Hönl's formula (James, 1954)

	Cu $K\alpha$		Cr $K\alpha$	
	$\Delta f'$	$\Delta f''$	$\Delta f'$	$\Delta f''$
V	0·2	2·3	−4·4	0·6
S	0·3	0·5	0·3	1·1
O	< 0·1	< 0·1	< 0·1	< 0·1
N	< 0·1	< 0·1	< 0·1	< 0·1
C	< 0·1	< 0·1	< 0·1	< 0·1

Assumption of the coordinates as obtained from the Patterson function, $x = \frac{1}{4}$ and $z = 0$, gave $\cos 2\pi\mathbf{H}.\Theta_V = \pm 1$ for reflexions with h and l both even, and $\cos 2\pi\mathbf{H}.\Theta_V = 0$ for those with h and l both odd. A plot of $|F_{\mathrm{Cr}}|$ against $|F_{\mathrm{Cu}}|$ for reflexions with h and l both even gave a straight line as expected, but for reflexions with h and l both odd $|F_{\mathrm{Cu}}| \neq |F_{\mathrm{Cr}}|$, showing that the vanadium coordinates were incor-

Table 2. *Observed structure factors together with their signs as determined by the different methods*

○ indicates sign indeterminate

hkl	F_{Cu}	F_{Cr}	*a*	*b*	*c*	*d*
0,0,2	55	41	+	+	+	+
4	65	52	+	+	+	+
6	151	169	+	+	−	−
8	55	41	+	+	+	+
10	32	37	+	+	−	−
12	83	81	+	+	○	+
2,0,0	77	53	−	−	−	−
2	31	15	−	−	−	−
4	228	220	−	−	−	−
6	69	56	−	−	−	−
8	80	76	−	−	−	−
10	34	43	−	−	+	+
4,0,0	94	63	+	+	+	+
2	108	67	+	+	+	+
4	90	103	+	+	−	−
8	25	33	+	+	−	−
10	96	81	+	+	+	+
6,0,0	133	129	−	−	−	+
4	61	67	−	−	+	+
6	116	85	−	−	−	−
8	47	54	−	−	+	+
8,0,0	159	117	+	+	+	+
2	111	80	+	+	+	+
10,0,2	45	38	−	−	−	+
12,0,0	92	49	+	+	+	+
2	72	47	+	+	+	+
4	94	55	+	+	+	+
−2,0,2	39	18	−	−	−	−
4	64	43	−	−	−	−
6	13	27	−	−	+	+
10	43	60	−	−	+	+
12	51	42	−	−	−	−
−4,0,2	137	124	+	+	+	+
4	121	126	+	+	−	−
6	81	67	+	+	+	+
8	45	32	+	+	+	+
10	76	65	+	+	+	+
−6,0,2	225	228	−	−	+	−
4	130	111	−	−	−	−
6	110	84	−	−	−	−
8	37	47	−	−	+	+
−8,0,2	129	106	+	+	+	+
4	37	26	+	+	+	+
6	66	41	+	+	+	+
10	103	83	+	+	+	+
−10,0,2	143	129	−	−	−	−
4	149	151	−	−	○	−
8	31	46	−	−	+	+
−12,0,2	80	82	+	+	○	−
1,0,3	23	14	○	−	−	−
5	45	33	○	−	−	−
9	45	33	○	−	−	−
11	66	35	○	−	−	−
3,0,3	93	74	○	+	+	+
5	7	18	○	+	−	−
7	71	61	○	+	+	+
11	47	35	○	+	+	+
5,0,1	20	20	○	−	○	+
7	71	40	○	−	−	−
7,0,1	52	37	○	+	+	+
9,0,5	47	29	○	−	−	−
11,0,3	76	45	○	+	+	+
−1,0,7	16	26	○	+	−	−
9	39	33	○	+	+	+
−3,0,3	14	29	○	−	+	−
5	37	24	○	−	−	−
7	38	27	○	−	−	−
9	45	33	○	−	−	−
11	34	35	○	−	○	−
−5,0,1	22	19	○	○	○	−
7	34	30	○	+	+	+
−9,0,1	41	38	○	○	○	−

rect. A Patterson projection with $(|F_{\mathrm{Cu}}(h0l)|-|F_{\mathrm{Cr}}(h0l)|)^2$ as coefficients showed that a small shift of the vanadium atom, to $x=0{\cdot}252$, $z=0{\cdot}016$, was required.

The plot of $|F_{\mathrm{Cu}}|/|\cos 2\pi(0{\cdot}252h+0{\cdot}016l)|$ *versus* $|F_{\mathrm{Cr}}|/|\cos 2\pi(0{\cdot}252h+0{\cdot}016l)$ gave a good straight line (Fig. 1), from which the signs of 65 out of a possible 72 reflexions were determined. The Fourier synthesis calculated with the use of these signs gave sufficient detail for the projection to be solved (Fig. 2*c*); the projection was refined by Fourier and least-squares methods and the solution extended to three dimensions by conventional means.

The electron-density maps calculated with signs from the vanadium at $x=0{\cdot}252$, $z=0{\cdot}016$ (Fig. 2*b*), and using signs from the final three-dimensional refinement (Fig. 2*d*) are shown for comparison.

Table 3. *Analysis of correctness of the signs*

	h+*l* even			*h*+*l* odd			All reflexions		
	a	*b*	*c*	*a*	*b*	*c*	*a*	*b*	*c*
Correct	34	34	43	0	18	18	34	52	61
Incorrect	15	15	3	0	3	1	15	18	4
Indeterminate	0	0	3	23	2	4	23	2	7
N	39	39	82	0	65	74	26	47	79

The magnitudes of the structure factors as observed with Cu *Kα* and Cr *Kα* are shown in Table 2 along with their signs as determined from (*a*) vanadium at 0·25, 0·00; (*b*) vanadium at 0·252, 0·016; (*c*) anomalous scattering; (*d*) the final refinement. An analysis of the correctness of the signs, as determined by the various methods, is given in Table 3; the signs from the final refinement are assumed to be the correct ones. The value N is defined as the percentage of correct signs minus the percentage of incorrect signs.

Conclusion

This work shows that despite smallness of the change in scattering factor caused by anomalous dispersion and unavoidable inaccuracy in the observations caused by background radiation, this effect may be used for phase determination, even with visually estimated data.

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The Crystal Structure of bis-(*N*-isopropylsalicylaldiminato)nickel(II)

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The crystal structure of bis-(*N*-isopropylsalicylaldiminato)nickel(II), $[OC_6H_4CHNC_3H_7]_2Ni$, has been determined from three-dimensional X-ray diffraction data with Fe $K\alpha$ radiation. Cell dimensions are $a = 13{\cdot}219$, $b = 19{\cdot}697$, $c = 15{\cdot}140$ Å, $Z = 8$. Space group, *Pbca*.

The structure consists of discrete molecules in which nickel(II) exhibits a tetrahedral coordination configuration.

Introduction

The structures of coordination compounds of nickel(II) are of considerable interest because the ion is found to adopt several different coordination configurations: planar (*e.g.* Stewart & Lingafelter, 1959), octahedral (*e.g.* Stewart, Lingafelter & Breazeale, 1961), and tetrahedral (*e.g.* Venanzi, 1958). Evidence has recently been given (Sacconi, Orioli, Paoletti & Ciampolini, 1962; Sacconi, Paoletti & Ciampolini, 1963) which indicates that the nickel(II) ion has a tetrahedral coordination configuration in bis-(*N*-isopropylsalicylaldiminato)nickel(II) $[OC_6H_4CHNC_3H_7]_2Ni$. We have now completed (Fox, Lingafelter, Orioli & Sacconi, 1963) the three-dimensional X-ray diffraction investigation of the structure.

Experimental

Two batches of bis-(*N*-isopropylsalicylaldiminato)-nickel(II) were used and found to be identical. One batch was prepared at the University of Florence by the reaction between bis(salicylaldehydato)nickel(II) and isopropylamine in methanol solution. The other batch was prepared by Dr H. F. Bauer at the University of California at Los Angeles by the reaction between nickel(II) chloride and the Schiff base *N*-isopropylsalicylaldimine in aqueous ethanol.

Cell dimensions were determined from a rotation and a zero-level Weissenberg photograph taken about the c axis with Fe $K\alpha$ radiation ($\lambda = 1{\cdot}9373$ Å). For calibration of the films the rotation pattern of NaCl ($a_0 = 5{\cdot}6387$ Å) was superimposed on each diffraction pattern. The cell dimensions are:

$$a = 13{\cdot}219 \pm 0{\cdot}006,\ b = 19{\cdot}697 \pm 0{\cdot}008\ ,$$
$$c = 15{\cdot}140 \pm 0{\cdot}018\ \text{Å}\ .$$

The cell contains eight molecules; observed density, $1{\cdot}31$ g.cm^{-3}, calculated $1{\cdot}32$ g.cm^{-3}. Systematic absences of $0kl$ for k odd, $h0l$ for l odd, and $hk0$ for h odd indicate the space group to be *Pbca*.

The crystal chosen for collection of intensities was a needle having dimensions $0{\cdot}22 \times 0{\cdot}14 \times 1{\cdot}22$ mm. Equi-