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The Crystal Structure of Nickel Carbonyl, $Ni(CO)_4$*

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The crystal structure of nickel carbonyl has been determined. Single-crystal oscillation diagrams have been obtained at $-55\pm5°$ C. These have been indexed on the basis of a cubic unit cell with $a_0 = 10{\cdot}84\pm0{\cdot}02$ Å. There are 8 molecules per unit cell. The most probable space group is $Pa3$.

Electron-density projections indicate that the configuration of the molecule is that of a regular tetrahedron. The analysis of one- and two-dimensional sections of three-dimensional Fourier syntheses indicates the following bond lengths: Ni–C = $1{\cdot}84\pm0{\cdot}03$ Å, and Ni–O = $2{\cdot}99\pm0{\cdot}03$ Å. These are in good agreement with known values determined by means of electron diffraction. The calculation of the electron density along a cube diagonal indicates that the atomic arrangement is Ni–C–O and not the alternative possibility Ni–O–C.

Introduction

Nickel carbonyl is one of a large group of relatively simple compounds which, because they happen to be liquids or gases at room temperature, have not been investigated by X-ray diffraction methods. An early electron-diffraction study (Brockway & Cross, 1935; Crawford & Horowitz, 1948) indicated that the molecule is tetrahedral and that the bond lengths are Ni–C = $1{\cdot}82\pm0{\cdot}03$ Å; C–O = $1{\cdot}15\pm0{\cdot}02$ Å. Dipole-moment measurements (Sutton, New & Bentley, 1933) show the Ni–C–O grouping is linear. Wells (1949), however, has pointed out that the generally accepted Ni–C–O configuration has not been unequivocally established to the exclusion of the alternative, Ni–O–C.

This paper reports the results of an X-ray diffraction investigation of crystalline nickel carbonyl. These furnish independent determinations of molecular configuration and bond lengths. They show that the carbon, and not the oxygen, atoms are adjacent to the nickel atoms.

Experimental

$Ni(CO)_4$ is a colorless, inflammable, toxic liquid which freezes at $-25°$ C. and boils at 42° C. Its thermal properties at temperatures lower than 0° C. have not been investigated and solid-phase transitions, if they exist, are unreported. The density of the solid has also not been reported up to now.

Specimens were prepared for X-ray use by vacuum distillation of small quantities of nickel carbonyl into thin-walled pyrex glass capillaries from 0·2 to 0·5 mm. inside diameter. The low-temperature single-crystal oscillation camera used in this investigation has been described elsewhere (Post, Schwartz & Fankuchen, 1951). A powder camera, 71·6 mm. in radius, was also adapted to low-temperature studies and was used for the determination of lattice constants.

Optical examination of single crystals from $-150°$ C. to $-25°$ C. gave no indication of solid-phase transitions in this temperature range. Except for one powder diagram obtained at $-100°\pm5°$ C., all powder and single-crystal diagrams were obtained at $-55°\pm5°$ C. A measure of the coefficient of expansion of the solid is furnished by differences in spacings between the $-55°$ C. and $-100°$ C. diagrams.

Unfiltered copper radiation was used, the nickel atoms in the specimen acting as a filter. Intensities of single-crystal reflections were estimated visually, using multiple-film techniques (Robertson, 1943). The usual Lorentz and polarization corrections were applied. The single crystals studied were cylindrical in shape and their diameters were less than half the optimum thickness; absorption corrections were therefore considered unnecessary.

In computing structure factors, the atomic scattering factor of nickel was corrected for the change in scattering power caused by dispersion by K electrons (James, 1950, pp. 182 and 608).

Experimental results

All reflections on single-crystal diagrams were indexed on the basis of a cubic unit cell ($a_0 = 10{\cdot}84\pm0{\cdot}02$ Å at $-55°\pm5°$ C.). (The lattice constant was determined using a 71·6 mm. radius powder camera; corrections for film shrinkage were applied.) The lattice constant at $-100°\pm5°$ C. is $10{\cdot}78\pm0{\cdot}02$ Å.

Some of the single crystals showed what appeared to be extremely weak birefringence between crossed polaroids. The cause of the birefringence could not be determined. Since several of the crystals shattered unexpectedly during X-ray exposures, it is possible that the observed birefringence resulted from strain

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in the crystals. Within the limits of experimental error, however, measurements of the lattice constants and intensities indicated that the crystals were cubic; although the possibility of the structure being only pseudo-cubic cannot be ruled out completely. There was no detectable splitting of the 'cubic' powder lines, and careful intensity measurements showed threefold symmetry about the [111] axis.

The volume of the unit cell is 1280 Å^3. The assumption that each unit cell contains eight molecules of nickel carbonyl leads to a calculated density of 1·77 g.cm.$^{-3}$ at $-55°$ C. The approximate density of crystalline nickel carbonyl at $-55°$ C. was found to be 1·7 g.cm.$^{-3}$; this estimate is based on extrapolation from the known density of the liquid at room temperature (Mellor, 1925, p. 953) to the freezing point, and on measurements of the contraction of the liquid in a capillary on freezing.

Reflections of the following types were absent: ($hk0$) with h odd, ($0kl$) with k odd, ($h0l$) with l odd.

An apparent fourfold symmetry about the cube edge was noted in the X-ray diagrams. However, careful re-investigation of intensities revealed small but unmistakable deviations from fourfold symmetry. The most probable space group is, therefore, $Pa3$. $Pm3$, $P23$ and $P2_13$ are also possible if the noted extinctions are not all systematic.

A Patterson projection onto the (001) plane was helpful in locating the positions of the nickel atoms and in eliminating ambiguities concerning the space group (Fig. 1). The heavy peaks at (0, 0), (0·500, 0), (0, 0·260), (0·250, 0·242), (0·500, 0·260) and (0·250, 0·500) are evidently Ni–Ni peaks. The relative heights of the peaks when scaled on an absolute basis confirm the conclusion that there are eight molecules per unit cell. Of the space groups listed above as possible, the 8-fold general positions of $Pa3$ are the only ones consistent with the nickel positions shown in the Patterson projection.

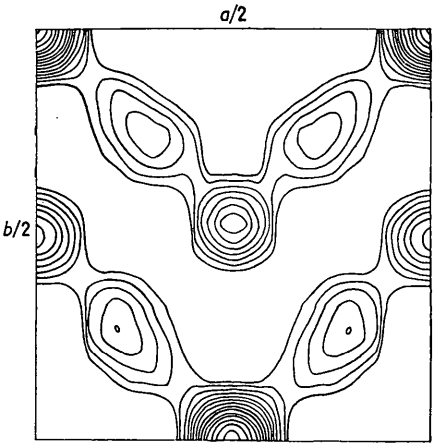

Fig. 1. Patterson projection on (001) plane.

There are no 32-fold general positions in $Pa3$. It is evident that the 32 carbon (and oxygen) atoms in the unit cell fall into two, crystallographically distinct, classes: one group in 24-fold and the other in 8-fold positions.

Two molecular configurations have been proposed for the $Ni(CO)_4$ molecule: one planar, and the other tetrahedral. The former is inconsistent with the point symmetry required of the molecule in this space group.

The signs of the nickel contributions to the structure factors, with nickel atoms at positions indicated by the Patterson projection, were used to compute an electron-density projection on a cube face. This showed the nickel peak along the diagonal at the assumed position; the co-ordinates of carbon and oxygen atoms could not be determined from the electron-density map. The individual carbon and oxygen peaks were not resolved. Resolution of these peaks was not anticipated, since the projected C–O distance is less than 0·7 Å (Hughes, 1941).

To locate the carbon and oxygen atoms, a systematic trial-and-error procedure was employed in which the parameters were varied so as to minimize the so-called 'reliability coefficient':

$$r = \Sigma||F_o|-|F_c||\div\Sigma|F_c| .$$

It was assumed that carbon and oxygen atoms were disposed about a central nickel atom in the configuration of a regular tetrahedron, and that Ni, C and O are collinear. Nickel atoms were assumed to be in the positions indicated by the trial Fourier analysis.

The location of the carbon and oxygen atoms then became a three-parameter problem. The variables are: p, the Ni–C distance; q, the Ni–O distance; and w (the angle through which the plane passing through the 24-fold positions, perpendicular to the body diagonal of the unit cell, is rotated). When $w = 0$, the projected carbon and oxygen positions are at the corners of squares. In that case, however, the ($hk0$) zone would show fourfold symmetry for all reflections for which h and k are even. Since such symmetry is not observed, $w \neq 0$. The presence of 'pseudo' fourfold symmetry indicates that w is probably small.

To determine the parameters p, q and w, it was assumed that

$$1{\cdot}80 \le p \le 1{\cdot}90;\ \ 2{\cdot}96 \le q \le 3{\cdot}02;\ \ -10° \le w \le 10° .$$

These limits are indicated by the electron-density map (and were subsequently confirmed by three-dimensional syntheses).

In testing a set of parameters p, q and w, the unobserved F's were calculated and the requirement that the calculated F's be zero or very small was set up. With a fixed p and q, F_c was plotted as a function of w for planes (220), (660), (410), (450), (810), (830), (240) and (460). (These reflections, as indicated in Table 1, were not observed.) It was found that in trying different sets (p, q) the angle w, which minimized the calculated structure factors for the unobserved reflections, did not vary appreciably from $-3°$. With

Table 1. *Comparison of* F_{hkl} *calculated and observed for* Ni(CO)$_4$

hkl	F_c	$\|F_o\|$
000	749	—
020	3	7
040	59	66
060	15	16
080	80	89
0,10,0	8	—
210	−108	125
220	1	—
230	−163	165
240	13	—
250	59	76
260	13	—
270	39	43
280	7	10
290	−56	48
2,10,0	6	—
2,11,0	−43	43
410	13	—
420	6	13
430	−14	12
440	217	197
450	6	—
460	4	—
470	3	17
480	64	68
490	2	—
610	87	83
620	10	—
630	6	33
640	0	12
650	84	81
660	2	—
670	−95	84
680	8	—
810	2	—
820	12	—
830	4	—
840	−65	67
850	6	—
860	3	—
870	2	—
880	41	28
10,1,0	−47	47
10,2,0	9	—
10,3,0	−55	39
10,4,0	5	—
10,5,0	1	—
10,6,0	0	—
10,7,0	1	—
10,8,0	2	—
111	65	78
121	−101	96
131	−55	61
141	23	27
151	−60	61
161	49	55
171	40	37
181	18	15
191	23	26
1,10,1	−31	26
1,11,1	−11	18
221	8	—
231	80	81
241	50	31
251	39	58
261	9	—
271	−33	28
281	28	—
291	−49	33
2,10,1	6	—
321	−92	99
331	67	60
341	10	—
351	44	36
361	29	32
371	−17	20
381	12	—
391	−17	20
3,10,1	−32	21
3,11,1	8	17
421	106	96
431	6	—
441	12	10
451	27	40
461	−51	52
471	33	—
481	5	—
491	6	—
4,10,1	27	27
521	40	57
531	25	42
541	34	35
551	33	34
561	−61	*
571	−33	24
581	21	—
591	−18	14
621	11	—
631	−32	29
641	16	—
651	−72	*
661	2	—
671	38	40
681	5	—
721	41	35
731	0	—
741	21	20
751	6	—
761	−52	18
771	9	20
781	13	—
821	−47	57
831	13	28
841	2	—
851	14	—
861	41	23
921	−34	31
931	−52	21
941	11	—
951	14	—
961	9	—
971	2	—
981	13	—
991	14	17
10,2,1	8	—
10,3,1	31	22
11,2,1	−28	35
222	−312	253
232	6	—
242	2	—
252	7	—
262	−54	51
272	1	—
282	14	—
292	3	41
2,10,2	23	15
332	40	44
342	59	70
352	−58	56
362	2	—
372	−55	54
382	−51	50
392	15	15
3,10,2	6	—
432	− 8	22
442	1	—
452	47	48
462	0	—
472	25	27
482	6	—
492	18	21
4,10,2	2	—
4,11,2	14	18
532	70	66
542	−71	70
552	−54	51
562	0	—
572	−40	46
582	39	30
592	24	16
632	0	—
642	5	—
652	13	—
662	15	—
672	4	—
732	−49	47
742	−63	75
752	25	23
762	5	—
772	19	18
782	35	29
792	−19	22
832	20	17
842	5	—
852	37	21
862	2	15
872	31	—
882	2	—
892	23	19
932	−20	26
942	24	21
952	29	—
962	2	—
972	27	22
10,3,2	5	—
10,4,2	3	—
11,4,2	26	16

Table 1 (*cont.*)

hkl	F_c	$\lvert F_o \rvert$
333	−12	27
343	31	22
353	−41	34
363	78	64
373	23	17
383	22	—
393	13	21
3,10,3	7	14
3,11,3	12	17
443	2	—
453	4	—
463	−95	96
473	23	21
483	8	—
493	− 3	21
4,10,3	19	30
4,11,3	9	16
543	3	19
553	29	28
563	18	27
573	9	22
583	12	—
593	17	17
643	3	—
653	−23	26
663	0	—
673	10	16
683	4	—
693	48	21
743	—	—
753	29	19
763	8	16
773	20	—
783	19	—
793	9	—
7,10,3	25	14
7,11,3	3	8
843	− 8	22
853	5	—
863	32	24
873	30	17
883	2	—
943	8	36
953	23	—
963	32	17
10,4,3	5	
10,5,3	29	20
10,6,3	1	—
10,7,3	−21	14
11,4,3	0	—
11,5,3		—
11,6,3	21	11
444	44	68
454	4	—
464	8	—
474	4	—
484	55	52
554	9	24
564	15	—
574	3	—
654	43	29
664	0	—
674	15	—
754	0	—
764	8	34
774	2	—
854	2	—
864	5	—
874	0	—
884	39	36
954	1	—
964	6	34
974	6	—
10,5,4	42	30
10,6,4	0	—

— Reflection not observed.
* Could not be distinguished.

$w = -3°$, and q held fixed at 2·99 Å, structure factors were calculated for $p = 1{\cdot}88$, 1·86, 1·84, 1·82 and 1·80 Å. A minimum set of F's for the unobserved reflections occured for $p = 1{\cdot}84$ Å. It was apparent that a small change in the assumed value of q would not alter appreciably the correlation between F_o and F_c. The reliability coefficient was computed for $F(p, q, w) = F(1{\cdot}84, 2{\cdot}99, -3°)$ and found to be 14·7% for the $hk0$ zone. These results do not uniquely establish the parameters but served as a starting point for three-dimensional work.

An electron-density projection onto the cube face is shown in Fig. 2. The signs of the observed F's were computed assuming $F_c(p, q, w)$ with $p = 1{\cdot}84$, $q = 2{\cdot}99$ and $w = -3°$. The arrangement of atoms in this projection is shown in Fig. 3. In this drawing

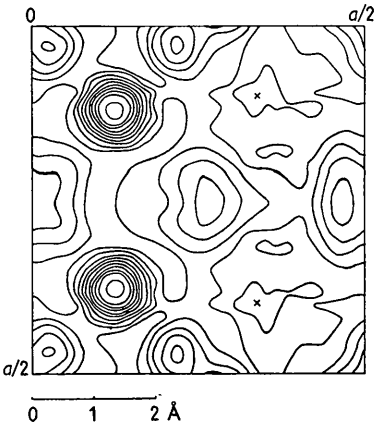

Fig. 2. Electron-density projection on (001) plane. Each contour line represents 3 e.Å^{-2}.

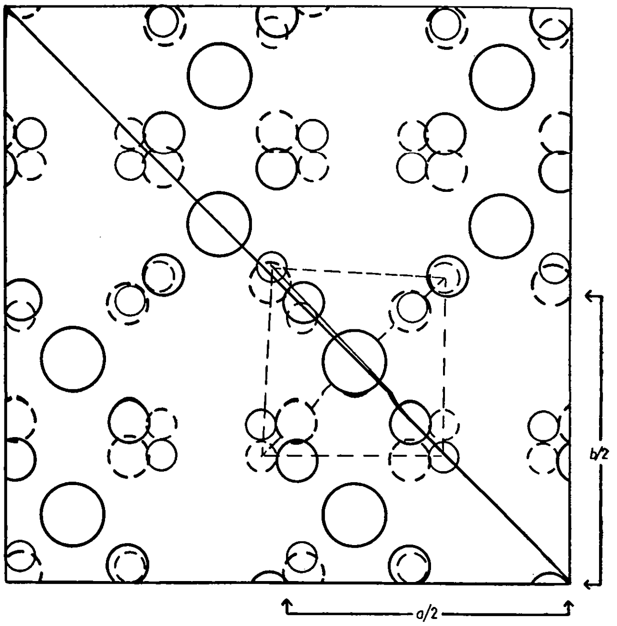

Fig. 3. Arrangement of atoms in one unit cell projected on cube face. Origin is at center of drawing. The quadrilateral indicates one molecule in projection.

the scale of the atomic radii is one-half the effective radii of neutral atoms as given by Goldschmidt (*Handbook of Chemistry and Physics*, 1949, pp. 2680–2). The origin of the unit cell is at the center of the drawing. The broken line of quadrilateral configuration represents one $Ni(CO)_4$ molecule in projection; the carbon and oxygen atoms drawn in solid circles are above the carbon and oxygen atoms drawn in broken-line circles. The region shown in Fig. 2 is outlined in the lower right-hand corner of Fig. 3.

The electron density along a cube diagonal was then calculated. Each cube diagonal passes through a vertex and center of each of two $Ni(CO)_4$ tetrahedra (i.e. through a nickel, carbon and oxygen atom of each tetrahedron). Signs for this Fourier synthesis were computed on the basis of atomic positions derived from the two-dimensional synthesis discussed above. All observed reflections were used in this summation. However, the available single-crystal data consisted only of oscillation diagrams about (100). (Other orientations of single crystals could not be obtained and powder diagrams were unsuited for intensity measurements.)

The observed reflections did not represent a spherical section of reciprocal space. In particular, reflections of higher order along, or close to [111] were missing; no reflections (hkl) with h, k and l all > 5 were observed or used in this summation.

The electron density along the cube diagonal, computed from the above data, is shown by the black line in Fig. 4. Bond lengths determined from this summation are:

$$\text{Ni–C} = 1{\cdot}65 \text{ Å}, \ \text{Ni–O} = 2{\cdot}99 \text{ Å} .$$

The Ni–O bond length agrees with that determined using two-dimensional data; the Ni–C bond length, however, is 0·19 Å less than that previously determined.

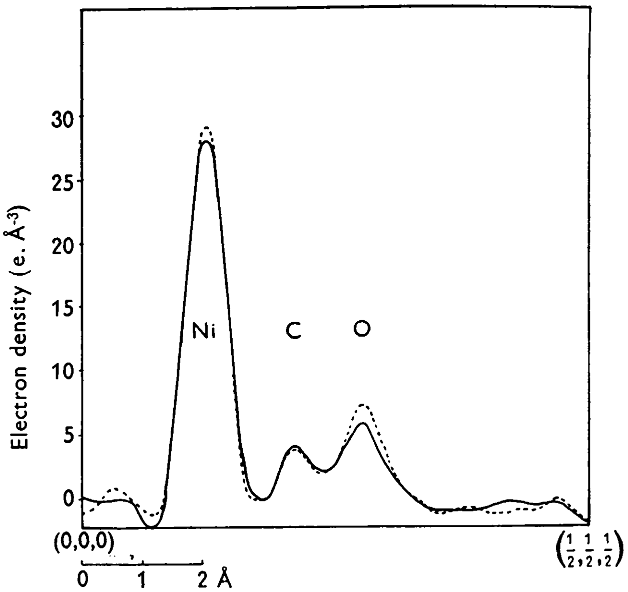

Fig. 4. Distribution of electron density along body diagonal.

It was felt that this discrepancy resulted from the systematic omission from the summation of reflections with h, k and l all > 5. A Fourier summation was then made, using values of F_{hkl} *calculated* (on the basis of Ni–C = 1·84 Å, Ni–O = 2·99 Å, $w = -3°$) for the same reflections used in the electron-density calculation. The results of this F_c summation are shown by the broken curve in Fig. 4. The two summations give essentially the same result.

A summation was then made using values of F_{hkl} calculated including all (hkl)'s with h, k and l not all > 9. The results of this summation show the nickel and oxygen atoms again in the assumed positions and the Ni–C distance as 1·81 Å. It is apparent that the anomalous Ni–C distance found in the original F_o summation results from the lack of full three-dimensional data and that had reflections of higher order been observed the representation of the electron-density distribution would have had its peaks shifted in the direction indicated by the more complete F_c summation. The close agreement of the F_c summation and F_o summation for the same number of reflections indicates the correctness of the assumed atomic positions.

The relative heights of the peaks in Fig. 4 agree with the conclusion that the carbon atom is bonded to the nickel atom and that the configuration is Ni–C–O, a conclusion which appears certain in view of the favorable correlation coefficients obtained with the structure postulated. It should be noted that the curve for the calculated data is steeper at the nickel peak. If the scaling factor is increased, the observed carbon peak is less than the calculated one, and the calculated data curve is in better agreement with Ni and O maxima on the observed data curve. This would seem to indicate a smearing-out of the carbon atom. Such a spreading should be anticipated in view of the collinearity of all four carbon bonds. Since the Hartree scattering factors assume spherical symmetry, the height difference of the calculated and observed curves may reflect the unsuitability of the scattering factors used in computing the calculated curve.

To test further the validity of the Ni–C–O conclusion and in order to see whether the relative heights of the peaks indicated were 'forced' by the computation of signs on the basis of the Ni–C–O configuration, signs were re-computed on the basis of Ni–O–C (by multiplying the original carbon and oxygen contributions to the total structure factors by 8/6 and 6/8 respectively). Of 159 structure factors, the signs of 158 (much to our surprise) remained unchanged. The remaining F_o when added to the section, did not influence the peak heights.

The electron density in a section perpendicular to a body diagonal and passing through the point (−0·025, −0·044, 0·280—the position of a 24-fold oxygen atom) was then computed. This yielded essentially the same bond lengths as had the line synthesis, and for the same reasons: the lack of full three-dimensional data. This section showed clearly one feature which previously had to be assumed: the nickel, carbon and oxygen atoms are collinear. In addition, the section showed that the angle w is $-3°$, as was previously calculated on the basis of the two-dimensional Fourier syntheses and consideration of absent reflections. The value of β (the 'temperature factor') in $F = KF_c \exp[-\beta(\sin\theta/\lambda)^2]$ was found to be 3·1 Å².

Calculated and observed structure factors are listed in Table 1.

The reliability coefficient for all *hkl*'s is 23%; it is 15% for the *hk*0 zone (equatorial-layer reflections), 21% for *hk*1, 19% for *hk*2, and increases for upper layers. Unobserved reflections were omitted from the above calculations. To establish an alternative figure of merit, unobserved reflections within the available volume of the reciprocal lattice, were included on the basis that their value was one-half the weakest reflection observed per layer. On this basis '*r*' is 28% for all *hkl*'s.

Discussion of the structure

Atomic positions are listed in Table 2. Bond lengths are:

$$\text{Ni–C} = 1{\cdot}84 \pm 0{\cdot}03\ \text{Å}\,,$$
$$\text{C–O} = 1{\cdot}15 \pm 0{\cdot}03\ \text{Å}\,.$$

The results of this investigation confirm the tetrahedral configuration and the bond lengths reported by Brockway & Cross (1935) on the basis of electron-diffraction measurements. The small differences between the bond lengths reported by Brockway & Cross and those given here are probably not significant.

The results of the Fourier synthesis show that the carbon atoms are bonded to a central nickel atom in the molecule; i.e. the configuration is Ni–C–O. The packing of molecules is similar to that of tin tetraiodide described in *Strukturbericht* (1931). Distances of shortest intermolecular approach are:

$$\text{Ni–Ni} = 4{\cdot}61\ \text{Å}\,,$$
$$\text{O–O} = 3{\cdot}24\ \text{Å}\,.$$

Table 2. *Atomic positions for* $Ni(CO)_4$

8 Ni in (*c*): $\pm(u, u, u;\ \tfrac{1}{2}+u, \tfrac{1}{2}-u, \bar{u};\ \circlearrowright)$
8 C in (*c*): C^{I}: $\pm(v, v, v;\ \tfrac{1}{2}+v, \tfrac{1}{2}-v, \bar{v};\ \circlearrowright)$
8 O in (*c*): O^{I}: $\pm(w, w, w;\ \tfrac{1}{2}+w, \tfrac{1}{2}-w, \bar{w};\ \circlearrowright)$
24 C in (*d*): C^{II}: $\pm(v_1, v_2, v_3;\ \circlearrowright;\ \tfrac{1}{2}+v_1, \tfrac{1}{2}-v_2, \bar{v}_3;$
$+;\ \tfrac{1}{2}-v_1, \bar{v}_2, \tfrac{1}{2}+v_3;\ \circlearrowright;$
$\bar{v}_1, \tfrac{1}{2}+v_2, \tfrac{1}{2}-v_3;\ \circlearrowright)$.
24 O in (*d*): O^{II}: $\pm(w_1, w_2, w_3;\ \circlearrowright;\ \tfrac{1}{2}+w_1, \tfrac{1}{2}-w_2, \bar{w}_3;$
$\circlearrowright;\ \tfrac{1}{2}-w_1, \bar{w}_2, \tfrac{1}{2}+w_3;\ \circlearrowright;$
$\bar{w}_1, \tfrac{1}{2}+w_2, \tfrac{1}{2}-w_3;\ \circlearrowright)$

with $u = 0{\cdot}123$ $v = 0{\cdot}220$ $w = 0{\cdot}281$
$v_1 = 0{\cdot}032$ $w_1 = -0{\cdot}025$
$v_2 = 0{\cdot}020$ $w_2 = -0{\cdot}044$
$v_3 = 0{\cdot}220$ $w_3 = 0{\cdot}280$

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Sur le Groupe Spatial de la Cellulose

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An accurate X-ray technique, using monochromatic focused radiation, has been applied to the analysis of reflexions from different kinds of cellulose. It has been found that the 021 and 130 reflexions are accompanied by diffuse streaks, the second of which has been previously incorrectly interpreted as a 030 reflexion. There is no evidence of a true 030 reflexion and the space group $P2_1$ is confirmed.

Le modèle admis pour la cellulose à la suite des travaux de Meyer & Mark (1928) et Meyer & Misch (1937) a été établi grâce à la conjonction des données chimiques et des déductions tirées des diagrammes de rayons X.

Dans ce modèle, l'absence de tout plan de symétrie