

short contacts, the only one which occurs being actually a C-H...O hydrogen bond.

(c) There is a uniform density of packing, the 'knobs' of one chain going into the 'holes' between the other chains.

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## Structure of Poly-L-Hydroxyproline A

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The structure of poly-L-hydroxyproline A is worked out from X-ray powder and oriented film patterns. The polymer chains are packed in a hexagonal lattice with  $a = 12.3$  and  $c = 9.15$  Å. The space group is  $P3_1$ . The arrangement of the chains is shown to be very similar to that of poly-L-proline II. It is also shown that the fundamental unit of the structure requires three helices as in collagen. The correctness of the structure was also verified by intensity calculations. The agreement between the calculated and observed intensities is good. No further refinement is carried out in the absence of accurate intensity data.

### 1. Introduction

From the structural view point, poly-L-proline and poly-L-hydroxyproline are of special interest. Although proline is a normal component of many proteins, hydroxyproline is found characteristically in collagenous tissue proteins. These polymers as a consequence of being imino acids, can only contribute to hydrogen bonded structures through their C=O groups, since the nitrogen of the prolyl residues carry no hydrogen atoms. Also there is no free rotation between the imino group and the  $\alpha$  carbon atom and this restricts the configurational possibilities. In fact, the restricted rotation of the N-C $\alpha$  bond undoubtedly determines the way in which the proteins, collagen and gelatin which contain high proportions of these

imino acids, may form folded structures in the solid state or in solution. The detailed investigation of poly-L-proline II, reported in the previous paper, has shown that this polymer resembles collagen and gelatin in its X-ray pattern and high optical rotation. As the polar properties of the hydroxyl group of the hydroxyproline residue are supposed to play an important role in determining the behaviour of collagen and gelatin, an X-ray investigation of the structure of poly-L-hydroxyproline is of great interest.

Poly-L-hydroxyproline of high molecular weight has been synthesised recently by Katchalski *et al.* (1956). A sample of the polymer was kindly made available by Prof. Katchalski. A detailed study of the X-ray pattern and optical activity of this material made by

the author showed that there are two modifications, which have been named as *A* and *B* respectively. The form *A* is highly crystalline and gives a rich X-ray pattern with discrete reflections, whereas the form *B* obtained by adding water to form *A* and evaporating to dryness, is poorly crystalline and gives a highly disoriented picture without much detail. There are three or four diffuse reflections with a rather sharp reflection at 2.86 Å. The specific rotation of the modification *A* in acetic acid is  $[\alpha]_D^{27} = -260^\circ$  and that of *B* in water is  $[\alpha]_D^{27} = -400^\circ$ . Form *B* can be converted to form *A* by alcohol or an organic acid. A paper on the structural transformations of poly-imino acids as revealed by X-ray, optical activity and other studies will be published elsewhere.

In this paper the discussion is restricted to the structure of poly-L-hydroxyproline *A* as determined by X-ray diffraction powder and oriented film methods. It is found that the individual helix of poly-L-hydroxyproline very closely resembles the poly-L-proline II helix. However, in this case an individual chain no longer possesses an exact threefold screw axis symmetry, although there is a repetition after every three residues. But there are three such chains in the unit cell related by a threefold screw axis symmetry and held together by O-H...O, interchain hydrogen bonds. It is interesting to see that the fundamental unit in poly-L-hydroxyproline *A* requires three-chain helices as in collagen. Quite apart from stereochemical considerations, the correctness of the proposed structure has also been verified by calculations of X-ray reflection intensities.

## 2. X-ray diffraction and physico-chemical data

### (a) X-ray powder pattern

The polymer used for X-ray investigation had a molecular weight of the order of 10,000. The X-ray powder pattern, shown in Fig. 1, was obtained by enclosing the dry powder in a Lindemann tube. More number of powder lines were obtained in this case than in the powder pattern of poly-L-proline II. There

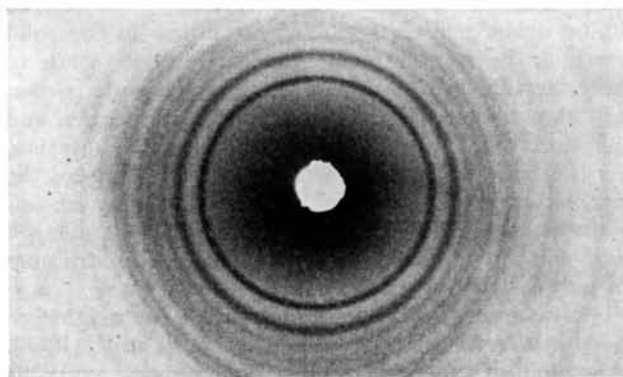


Fig. 1. X-ray powder pattern of poly-L-hydroxyproline *A* taken with a cylindrical camera of radius 5.73 cm.

are about 20 lines which can be observed and whose *d* spacings can be measured. The observed and calculated *d* spacings are given in Table 1. All the reflec-

Table 1. Observed and calculated *d* spacings of the reflections of poly-L-hydroxyproline *A*

No.	$d_o$ (Å)	$d_c$ (Å)	<i>hkl</i>
1	10.62	10.69	100
2	6.81	6.90	101
3	6.15	6.15	110
4	5.10	5.10	111
5	4.60	4.61	201
6	4.23	4.20	102
7	4.04	4.03	210
8	3.66	{ 3.65 3.68	{ 112 211
9	3.49	3.47	202
10	3.27	3.31	301
11	3.03	{ 3.02 3.05	{ 212 003
12	2.92	2.93	103
13	2.77	2.80	302
14	2.45	{ 2.44 2.46	{ 123 312
15	2.27	2.25	141
16	2.16	2.15	114
17	2.03	2.05	330

tions can be indexed on the basis of a hexagonal cell with  $a=12.3$  and  $c=9.15$  Å. There were no other systematic absences except 001, 002, 004, etc. There should therefore be a threefold screw symmetry about the *c* axis.

### (b) Preparation of oriented film and its X-ray pattern

The above results have been confirmed by X-ray diffraction patterns obtained with oriented films. Some difficulty was experienced in obtaining oriented films. The polymer is insoluble in the usual organic solvents, but readily dissolves in water and dichloroacetic acid. It is also soluble in hot formic acid. As already men-

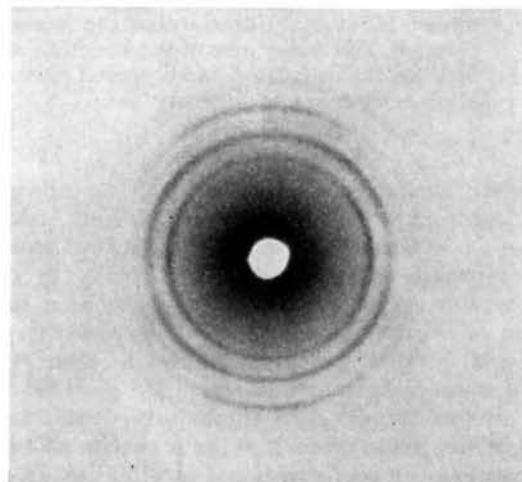


Fig. 2. X-ray diffraction pattern of oriented film of poly-L-hydroxyproline *A* with beam parallel to the film (taken with a flat plate camera and  $D=5$  cm.).

tioned the form *A* when dissolved in water is converted to form *B* which gives few diffuse reflections in its X-ray pattern. Attempts to get oriented films from a solution in dichloroacetic acid or formic acid were also unsuccessful. Therefore the polymer was dissolved in a minimum quantity of water (just a drop of water will be enough to dissolve a fairly large quantity of the polymer). To this, excess of acetic acid was added. The polymer was then precipitated with ether. The wet precipitate was immediately wiped out on a glass plate and allowed to dry. The film thus obtained showed orientation under the polarizing microscope. The X-ray pattern obtained with the oriented film is shown in Fig. 2. The dried precipitate gave exactly the same powder pattern as the original powder of form *A*, showing that the structure has not changed. The oriented pattern confirmed the indexing of the reflections and the symmetry of the unit cell.

### (c) Density

The density of the powder was determined by the floatation method using bromoform-benzene mixtures. The observed density was 1.40 g.cm.<sup>-3</sup> which is in good agreement with the calculated density, 1.43 g.cm.<sup>-3</sup>, for nine residues in the unit cell, each chain having three residues in the repeat distance of 9.15 Å.

### (d) Optical rotation

The specific rotation of poly-L-hydroxyproline has been measured in water and it is  $[\alpha]_D^{27} = -400^\circ$ . Owing to its insolubility in the usual organic solvents, no experiments could be performed in these solvents (Kurtz, Berger & Katchalski, 1958). The author has succeeded in measuring the specific rotation of form *A* in glacial acetic acid in the following way. The polymer was dissolved in a minimum quantity of water and then excess of glacial acetic acid was added to form the solution. The specific rotation obtained for poly-L-hydroxyproline in this medium was  $[\alpha]_D^{27} = -260^\circ$ . The value reported may not be very accurate as the available quantity was small and hence the concentration of the solution was also small. However, the rotation is much lower than  $-400^\circ$  reported for a solution in water by Kurtz *et al.* (1958). As already pointed out the powder precipitated with ether from the solution in acetic acid gave the same X-ray pattern as the original one. Thus the specific rotation of the form *A* in acetic acid is  $[\alpha]_D^{27} = -260^\circ$ .

### (e) Infrared spectrum

Recent work on the infrared spectra of poly-L-hydroxyproline indicates a sharp peak corresponding to a C=O stretching frequency at 1620 cm.<sup>-1</sup> (Kurtz, Fasman, Berger & Katchalski, 1958). The sharpness of the peak might indicate that the majority of the carbonyl groups participate in hydrogen bonding.

## 3. Derivation of the structure

### (a) Space group

As already mentioned, all the observed reflections could be indexed on the basis of a hexagonal cell with  $a = 12.3$  and  $c = 9.15$  Å, there being nine hydroxyproline residues per unit cell. A careful examination showed that it is not possible to have a smaller cell containing only three residues per unit cell.

If we suppose that the nine residues are equivalent, then, of all the possible space groups in the trigonal class, only the space group  $R\bar{3}$ , indexed on a hexagonal lattice, is possible. The general conditions for reflections to occur in that case are for  $hkl$ :  $-h+k+l=3n$  and for  $00l$ ,  $l=3n$  (*International Tables for X-ray Crystallography*, 1952). However, these conditions are not satisfied by the reflections observed with the polymer under study. For example, the 111 reflection, which is forbidden according to the above condition, is observed as a very strong reflection (Fig. 1) of the polymer. Moreover, this space group requires the presence of both simple threefold axes as well as threefold screw axes and there is little freedom in the disposition of the residues. Actually, it is found that, if the chains are packed with this symmetry, it is not possible to form decent hydrogen bonds between the hydroxyl groups and carbonyl oxygen atoms with the above unit cell dimensions.

Consequently, the structure must have a lower symmetry and there can only be three equivalent points

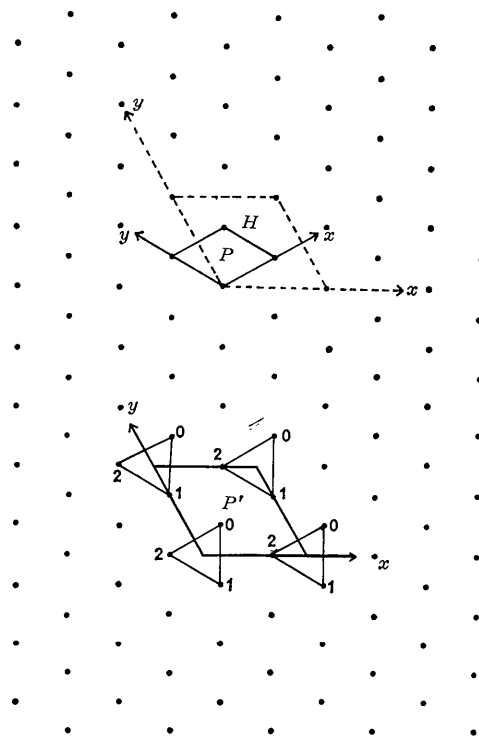


Fig. 3. Diagram showing the relation between *P*, *H* and *P'* cells.

in the unit cell. Thus, the nine residues must occur as three groups from the crystallographic point of view. A clue to the possible type of structure is provided by the following considerations. As is well known, a hexagonal lattice can also be indexed on the basis of a  $H$  lattice (*Internationale Tabellen zur Bestimmung von Kristallstrukturen*, 1935 Edn.). The condition for reflections to occur in the  $H$  lattice is  $h-k=3n$ . If this condition is fulfilled then it is equivalent to take a smaller unit cell  $P$ , as shown in Fig. 3. Each lattice point in this diagram corresponds to a single chain possessing a threefold screw axis symmetry. There will also be threefold screw axes mid-way between three chains (two such in the  $P$  cell). This is made particularly clear in Fig. 4, in which a cell  $P'$  is drawn having the same size as the  $H$  cell, but displaced such that its origin occurs mid-way between the chains represented by points.

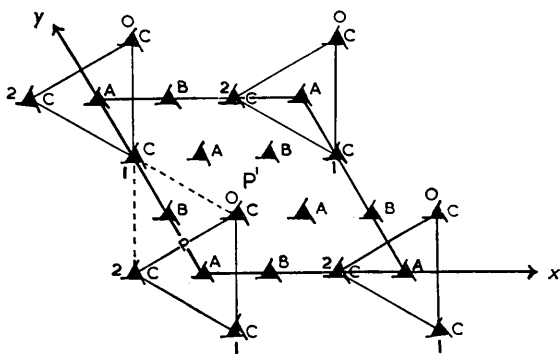


Fig. 4. The  $P$  and  $P'$  cells with the symmetry elements marked as  $A$ ,  $B$  and  $C$ . Note the origin of  $P'$  cell is mid-way between the chains represented by points.

Just like the  $H$  cell, the  $P'$  cell is also triply primitive and has three types of threefold screw axes designated by  $A$ ,  $B$  and  $C$  respectively in Fig. 4. The true unit cell is the  $P$  cell for this also. However, the evidence of the X-ray reflections completely rules out the smaller cell. It follows therefore that one (or more) of the symmetry elements in the  $P'$  cell must not be present. Suppose that the individual chains do not possess a screw symmetry axis i.e. the elements of symmetry  $C$  are absent. Then obviously either the screw axes  $A$  or  $B$  must also be absent. It is immaterial which is removed. We shall suppose that the  $B$  series are absent, so that we are left only with the threefold screw axes  $A$ , through the lattice points of the  $P'$  cell (Fig. 4).

This situation is also shown in the lower half of Fig. 3. The three chains in the unit cell are numbered 0, 1 and 2 and each has three residues per unit cell, but not related by a threefold screw axis, although this symmetry is approximately attained. However, the three chains are exactly related by threefold axes.

#### (b) Relation to poly-L-proline II structure

The choice of the  $P'$  (or  $H$ ) cell is also justified by a comparison of the X-ray patterns of poly-L-hydroxyproline  $A$  and poly-L-proline II. The X-ray patterns of the two polymers bear a general resemblance to each other. For example the two strong reflections in the case of poly-L-proline II are the 100 and 101 reflections. In the case of poly-L-hydroxyproline the strongest reflections are 110 and 111 at nearly the same spacings. These two pairs of reflections are thus similarly situated. In fact, they become equivalent if the latter indices are imagined to be indexed on an  $H$  cell, the primitive  $P$  cell being the one used for indexing the reflections of poly-L-proline II. Moreover, in the case of poly-L-hydroxyproline  $A$ , the 100 and 101 reflections are extremely weak, as observed in the powder diagram. Even if the structure amplitudes are small for these reflections, the intensities in the powder pattern will be considerable because of the multiplication of the square of the structure amplitude by Lorentz and polarization factors, which are very high at low Bragg angles. The L.P. factors for these two reflections are 383 and 158. Therefore it is concluded that the arrangement of the chains should be very close to that occurring in the structure of poly-L-proline II. Each chain in poly-L-hydroxyproline  $A$  no longer possesses exact symmetry but the deviation from the symmetrical position should be small. Three such chains are, however, related by a threefold screw axis and are arranged in the hexagonal cell  $P'$ . As the individual chains should necessarily be left-handed ones, the three chains should be related by the symmetry element  $3_2$  and hence the space group is  $P3_2$ .

#### (c) Derivation of atomic coordinates

The peptide group was assumed to be planar and to be in the *trans* configuration as in poly-L-proline II. Preliminary wire models based on Corey & Pauling's dimensions for the peptide group were constructed. The hydro ring was assumed to be planar, except for the carbon atom  $\gamma C$ , which was pushed away from the plane in the direction of the hydroxyl group to which it was attached, as found in the L-hydroxyproline structure by Donohue & Trueblood (1952). This is naturally to be expected because of the attraction by the OH group. Three chains were built and kept at positions related by the trigonal axes. To start with, the chains were assumed to possess threefold screw axis symmetry. The smallest cell required with an O-H...O bond distance of 2.5 Å was  $a=7.4$  Å, whereas the observed cell is smaller namely with  $a=7.1$  Å. Moreover there were severe short contacts between the  $\beta$  carbon of one chain and the oxygen of the hydroxyl group of another chain. Thus in order to fit in the nine residues within the observed unit cell, the configurations of the chains had to be changed slightly, modifying them so that the symmetry of the individual chains was destroyed. When this was done,

it was possible to obtain a satisfactory structure packed into the observed unit cell. It is interesting to note that the more symmetric arrangement is less densely packed and this may explain why the structure takes up a lower symmetry.

During the course of the investigation the height of the residues was varied from 2.90 to 3.20 Å such that the total height for three residues was  $c=9.15$  Å. The bond angle at the  $\alpha$  carbon atom between the bonds NC and CC' was also varied from  $105^\circ$  to  $115^\circ$ . The actual coordinates of the atoms of a single chain in each case was obtained accurately by graphical methods. Three chains were then kept at trigonal positions, such that there were no short contacts and hydrogen bonds were formed between the hydroxyl groups and carbonyl oxygen atoms. The distance between the chains was also varied from 7 to 7.5 Å within the unit cell of  $a=12.3$  Å, such that the arrangement closely resembled the  $P'$  cell.

This was actually done as follows: For a particular configuration of the chain, the atoms of the helix were projected on to the  $ab$  plane on a paper. Two more tracings of the projections were also obtained. Two such tracings marked as 0 and 2 in Fig. 5 were kept at positions related by trigonal axes and were separated by about 7 to 7.5 Å. The chains could be rotated about the  $c$  axis with the restriction that they should be related by the symmetry element  $3_2$ . The position and orientation of the chain of another unit marked as 1' (Fig. 5) was obtained such that good O-H...O hydrogen bonds were obtained.

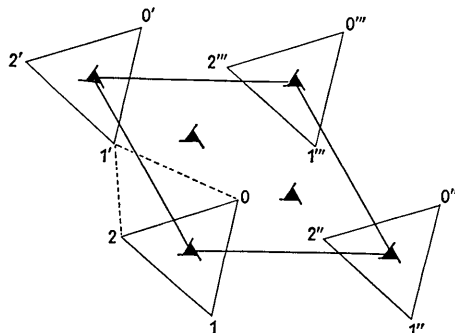


Fig. 5. The determination of the orientation of the chains in the unit cell. The chains marked 0, 1 and 2 no longer possess symmetry.

It was found that there were two or three arrangements for which hydrogen bonds of lengths 2.5 to 2.6 Å could be made if the hypro ring is slightly rotated about the CN bond as is found in N,N'-diglycyl-L-cystine dihydrate (Yakel & Hughes, 1954). Out of these, the arrangement shown in Fig. 6 was chosen, as the twist required for this purpose was least in this case. The arrangement is very similar to that found in the poly-L-proline II structure (Sasisekharan, 1959) and there are practically no short contacts of any sort. The coordinates of the atoms in a single chain (chain 0) for this arrangement are given in Table 2. The co-

Table 2. Coordinates of the atoms in a single chain (chain 0 of Fig. 6) containing three residues

Atom	$x$	$y$	$z$
$\alpha C_1$	0.320	0.435	0.330
$\beta C_1$	0.226	0.479	0.372
$\gamma C_1$	0.137	0.450	0.241
$\delta C_1$	0.169	0.333	0.172
$C'_1$	0.318	0.313	0.119
$N_1$	0.257	0.350	0.205
$O_1$	0.430	0.345	0.129
$OH_1$	0.206	0.552	0.139
$\alpha C_2$	0.444	0.352	0.667
$\beta C_2$	0.580	0.451	0.703
$\gamma C_2$	0.638	0.540	0.579
$\delta C_2$	0.526	0.543	0.507
$C'_2$	0.327	0.353	0.448
$N_2$	0.421	0.414	0.542
$O_2$	0.244	0.240	0.462
$OH_2$	0.676	0.472	0.479
$\alpha C_3$	0.234	0.223	0.000
$\beta C_3$	0.197	0.085	0.040
$\gamma C_3$	0.230	0.030	0.910
$\delta C_3$	0.347	0.145	0.840
$C_3$	0.355	0.343	0.787
$N_3$	0.319	0.247	0.874
$O_3$	0.321	0.423	0.798
$OH_3$	0.126	-0.057	0.808

ordinates of the atoms in the other two chains (1 and 2 respectively) are obtained by applying the symmetry operations of  $3_2$ . The residue heights in a single chain within a repeat of 9.15 Å are 3.05, 3.08 and 3.02 Å. The values for the bond angles, between NC and CC' at the  $\alpha$  carbon atoms of a single chain are  $107^\circ$ ,  $106^\circ$  and  $107^\circ$ . The other bond angles and bond distances are also given in Table 3, and it will be seen that the structure is quite satisfactory from the stereochemical point of view.

Table 3. List of bond lengths and bond angles

(a) Bond lengths and bond angles in a single hypro residue of the chain

Bond	Length	Atoms	Angles
$\alpha C_1-N_1$	1.47 Å	$C'_1-N_1-\delta C_1$ ...	$123^\circ$
$N_1-\delta C_1$	1.49	$\alpha C_1-N_1-\delta C_1$ ...	115
$\delta C_1-\gamma C_1$	1.52	$N_1-\delta C_1-\gamma C_1$ ...	105
$\gamma C_1-\beta C_1$	1.51	$\delta C_1-\gamma C_1-\beta C_1$ ...	104
$\beta C_1-\alpha C_1$	1.53	$\gamma C_1-\beta C_1-\alpha C_1$ ...	109
$\gamma C_1-OH_1$	1.46	$\beta C_1-\alpha C_1-N_1$ ...	105
		$\beta C_1-\alpha C_1-C'_2$ ...	113
		$\delta C_1-\gamma C_1-OH_1$ ...	108
		$\beta C_1-\gamma C_1-OH_1$ ...	106

The dimensions of the peptide group are as given in Corey & Pauling (1953).

(b) Intermolecular hydrogen bonds

Hydrogen bond lengths	Hydrogen bond angles
OH(0)-O(1')-2.50 Å	$104^\circ$
OH(1')-O(2)-2.53	108
OH(2)-O(0)-2.56	110

#### 4. Comparison between the X-ray data and calculated intensities

The intensities of all the possible reflections which can occur with  $d$  spacings larger than 1.80 Å were cal-

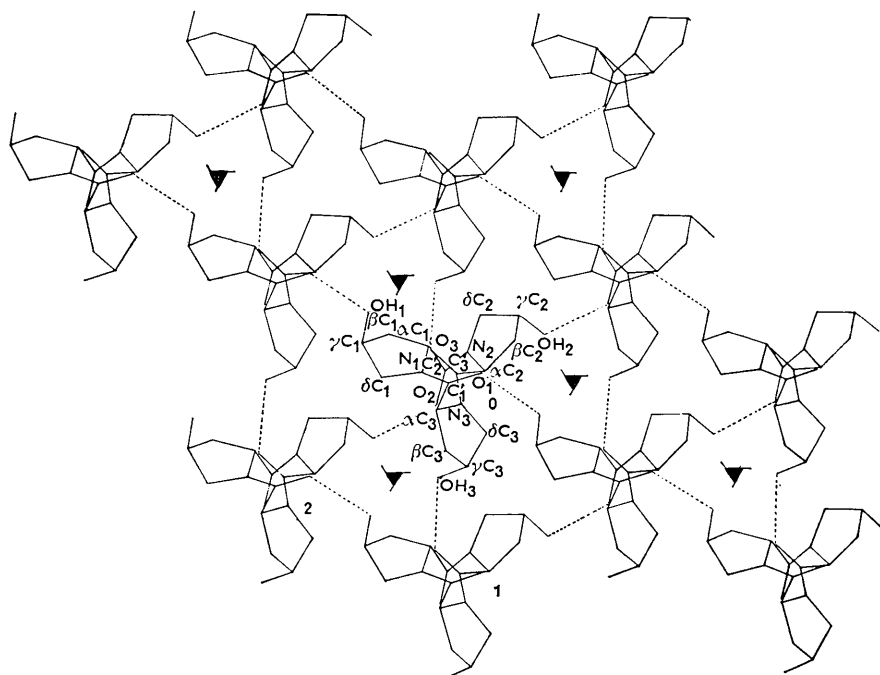


Fig. 6. The structure of poly-L-hydroxyproline A projected on the  $a, b$  plane. Hydrogen bonds are shown by dashed lines.

culated. There are 18 oxygen atoms, 9 nitrogen atoms and 45 carbon atoms in the unit cell. For the space group  $P3_2$ , the equivalent points are  $x, y, z$ ;  $y-x, \bar{x}, z+\frac{1}{3}$ ; and  $\bar{y}, x-y, z+\frac{2}{3}$ . The scattering factors for C, N and O atoms were taken from the reported values of Viervoll & Øgrim (1949). The calculated intensities have been multiplied by Lorentz and polarization factors. An isotropic temperature factor with  $B=4.0 \text{ \AA}^2$  has also been applied. The calculated values along with the observed intensities are given in Table 4.

### 5. Conclusion

On comparing the intensities there is seen to be good agreement between the calculated values and X-ray powder data. The calculated intensities for the reflections 100 and 101 are almost negligible. This is because of the fact that the arrangement is very very close to the  $P'$  cell (cf. Figs. 3 and 6). A slightly larger deviation from this arrangement will probably give a better agreement between the calculated and observed intensities, but in the absence of precise experimental data, further refinement was not considered worthwhile.

Referring to Fig. 6, it will be noticed that all the available carbonyl oxygen atoms and hydroxyl groups are bonded. The bond angles and the bond distances listed in Table 3 are within the normal values. The  $\text{O-H} \cdots \text{O}$  bond length  $2.5 \text{ \AA}$  is shorter than the value of  $2.6$  to  $2.9 \text{ \AA}$  usually reported for amino acids. But such short bond lengths have been reported in a few cases in crystal structure analyses. (Oxalic acid— $2.49 \text{ \AA}$ —Ahmed & Cruickshank, 1953; Urea oxalate—

Table 4. List of calculated and observed intensities of the reflections of poly-L-hydroxyproline A

The calculated intensities are multiplied by L.P. factors and a temperature factor with  $B=4 \text{ \AA}^2$

$hkl$	$I_o$	$I_c \times 10^{-3}$	$hkl$	$I_o$	$I_c \times 10^{-3}$
100	<i>vw</i>	—	312	} broad medium	122
101	<i>vw</i>	7	320		5
110	<i>s</i>	1590	213		108
200	—	6	321	—	5
111	<i>s</i>	1479	410	} <i>vw</i>	17
201	<i>m</i>	103	303		6
102	<i>m</i>	208	402		—
210	<i>m</i>	65	411	<i>w</i>	93
211	} <i>m</i>	34	104	—	1
112		9	223	—	2
300	—	41	322	—	6
202	<i>m</i>	149	114	<i>vw</i>	37
301	<i>m</i>	229	313	—	28
220	—	154	204	—	4
003	} <i>m</i>	4	412	—	9
212		207	330	<i>w</i>	25
310	—	9	420	—	2
103	<i>m</i>	127	403	—	9
221	—	5	214	—	3
131	—	8	331	—	13
302	<i>vw</i>	12	421	—	1
113	—	1	304	—	15
400	—	1	323	—	24
203	—	25	332	—	1
401	—	16	413	—	2
222	—	2	422	—	3
			224	—	16
			134	—	1

*s*—strong; *m*—medium; *w*—weak; *vw*—very weak

$2.50 \text{ \AA}$ —Donohue, 1952; Tyrosine hydrochloride and hydrobromide— $2.50 \text{ \AA}$ —Srinivasan, 1958.)

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## The Crystal Structure of $Ti_2Ni$

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The crystal structure of  $Ti_2Ni$  has been determined from powder specimens. The unit cell is face-centered cubic with 96 atoms and dimension  $a = 11.278 \pm 0.001 \text{ \AA}$  at  $21^\circ \text{C}$ . The space group is  $O_h^k-Fd3m$ . 64 titanium atoms are in positions 48f and 16c, and 32 nickel atoms are in positions 32e. The atomic parameters,  $X_{Ni} = 0.215 \pm 0.001$  and  $X_{Ti} = 0.810 \pm 0.002$ , were determined by trial and error.

### Introduction

Laves & Wallbaum (1939) stated that the  $Ti_2Ni$  phase had a complex face-centered cubic structure with 96 atoms per unit cell. No value of cell constant was given. Duwez & Taylor (1950) investigated several  $Ti_2X$  phases and found  $Ti_2Ni$  to be face-centered cubic with a density of  $5.77 \text{ g.cm.}^{-3}$  and lattice constant of  $11.310 \text{ kX. units}$ —giving 96 atoms per unit cell. Rostoker (1952) reported the structure for  $Ti_2Ni$  to be face-centered cubic ( $Fe_3W_3C$  type) and the cell side to be  $11.29 \text{ \AA}$ . Yurko *et al.* (1958) found the cell side to be  $11.278 \text{ \AA}$  at  $21^\circ \text{C}$ . The purpose of the present investigation was to obtain the complete crystal structure of the phase.

### Experimental

The stoichiometric alloy (33.33 at. % Ni) was prepared from iodide titanium and spectrographic standard nickel by levitation melting (Yurko *et al.*, 1958). The ingots were crushed and  $-200$  mesh particles were annealed at  $700^\circ \text{C}$ . and examined by both powder camera and Geiger diffractometer techniques using  $Co K\alpha$  radiation. The density was determined by the

pycnometer method on a 25 g. sample of the crushed and annealed powder, making the usual corrections. The cell constant was determined by methods previously described (Yurko *et al.*, 1958).

Intensity data were obtained by measuring with a planimeter the areas under reflection peaks on two diffractometer charts. Values obtained for the two charts generally agreed within 5%. An average figure was taken. The intensities of reflections too weak to be measured in this way were estimated from a powder photograph, taken with a Philips 11.483 cm. diameter camera of the Straumanis type. The estimation was made visually, by comparing the weak lines with slightly stronger reflections whose intensities had been measured on the diffractometer chart.

### Unit cell and space group

From the cell constant of  $11.278 \pm 0.001 \text{ \AA}$  and the measured density of  $5.723 \pm 0.001 \text{ g.cm.}^{-3}$ , the number of atoms per unit cell is evaluated at 96.0.

The systematic absences were found to obey the following rules: