III. *X-Ray Studies of the Structure of Hair, Wool, and Related Fibres. I.—General.*

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[Plates 2, 3.]

Introduction.

It is now some ten years since it was first realised that, in common with natural and artificial cellulose fibres, animal fibres with a protein basis are in many cases sufficiently crystalline to yield a pronounced interference figure when examined with monochromatic X-rays. Such " X-ray fibre diagrams " were reported in 1921 by Herzog and Jancke* for muscle, nerve, sinew, and hair, and in 1924 similar photographs from human hair were obtained by one of the present writers.† From an X-ray examination of wool it was concluded by Threadgold‡ that " there is no evidence for assuming the wool fibres and yarns examined to have a crystalline structure," but in 1927 Ewles and Speakman§ had already obtained wool interference figures precisely similar to those previously obtained from hair. The two last-named authors endeavoured to interpret their results in the light of certain physical properties, but it has since become clear that the problem of hair structure is sufficiently complex to necessitate an X-ray study of a wide range of materials under as great a variety of conditions as possible. The present communication is an account of the preliminary results of such an investigation.

Over a hundred X-ray photographs have been taken, using copper K-radiation filtered of the Kβ line by nickel foil about 1/100 mm. thick. The " slit " was a rectangular aperture, 4 cm. $\times$ $\frac{1}{2}$ mm., the scattered rays from which were screened off in the usual manner by a secondary slit. With this arrangement, a Shearer tube, and an unrectified

* " Festschrift der Kaiser Wilhelm-Gesellschaft," 1921.

† W.T.A.—For a series of lectures on " The Imperfect Crystallisation of Common Things," delivered by Sir William Bragg at the Royal Institution.

‡ " Publication 93 of the British Research Assoc. for Woollen and Worsted Industries," 1928.

§ " Leeds Meeting of the British Association," 1927 ; ' Nature,' vol. 122, p. 346 (1928) ; ' Proc. Roy. Soc.,' B, vol. 105, p. 600 (1930).

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transformer, photographs of bundles of hair 1 mm. thick may be obtained in 10 hours. The materials as yet examined are Geelong Merino wool of 80's quality (diameter 13 μ), Australian Merino wool of 64's quality (diameter 23 μ), English Cotswold wool (diameter 40 μ), human hair (diameter 70 μ), llama hair (diameter 110 μ), hedgehog spine (diameter 1 mm.), and porcupine quill (diameter 2 to 5 mm.). The Geelong, Australian, and Cotswold wools, and also the human hair, were taken from the actual specimens used by SPEAKMAN in his comprehensive researches on the load/extension curves of these fibres, so that in what follows there can be no doubt as to the legitimacy of any comparisons which may be drawn between X-ray effects and accompanying elastic behaviour.

The photographs show that without doubt a considerable proportion of the structure of hair* is crystalline or pseudo-crystalline, and that this constituent is common to all the fibres examined, in the sense that substantially the same X-ray photograph is always obtained, from the finest Merino wool to such large-scale structures as quills. In fact, the interference figures given by human hair and the tip-end of a porcupine quill, respectively, are practically indistinguishable. Presumably, we are dealing with a photograph of crystalline keratin, or of one of the forms of keratin, if indeed there is more than one fundamental keratin. It is immediately noteworthy that the dimensions of the photograph are not such as would be expected from a substance of very high molecular weight, of the order usually associated with proteins ; rather are we reminded of the case of cellulose, in which it seems clear that a comparatively simple unit may be repeated, " via " primary valency bonds, an indefinite number of times.

The second important result of the present investigation has been to show that the X-ray photograph of unstretched hair is quite different from that of stretched hair. On stretching the hair, the α-photograph, as we shall call it, fades away and is gradually replaced by the β-photograph, the interferences of which first become prominent at about 30 per cent. extension. The α-photograph is finally lost sight of at about 60 per cent. extension, at which point the β-photograph is almost as well defined as it is possible to obtain it by this method, since very soon after, in the neighbourhood of 70 per cent. extension, the fibres break.† The occurrence and progress of this transformation from the α-form to the β-form accounts readily for the main features of the characteristic load/extension curve, and for the marked changes which are brought about in the physico-chemical properties of hair on stretching.

The Low Tension Photograph.

Typical examples of the low tension photograph are shown in Plate 2, figs. 1, 2, 3, 4, and 5A. In each of these photographs the X-ray beam was perpendicular to a

* We shall use the word " hair " in its most general sense, and when necessary state the kind of hair being referred to.

† J. B. SPEAKMAN, ' J. Text. Inst.,' T, vol. 17, p. 457 (1926).

bundle of parallel fibres which were unstretched and under ordinary laboratory conditions of temperature and humidity. Preliminary experiments were made to determine the effect on the photographs of varying conditions of humidity, but it was concluded that if such an effect existed, it was of too small an order to warrant special precautions until more had been learned of the general structure and properties of the fibres. Detailed X-ray examination of the swelling properties of hair will be reported on later, but in the present communication it will be understood that all photographs are of hair under normal laboratory conditions.

The X-ray photographs of hair are not sufficiently well defined to justify at this stage anything more than a description of their salient features and the setting-up of a tentative unit cell. Fig. 1 is an ideal diagrammatic representation of the low tension photograph referred to the BERNAL chart for single crystal rotation photographs.* It should

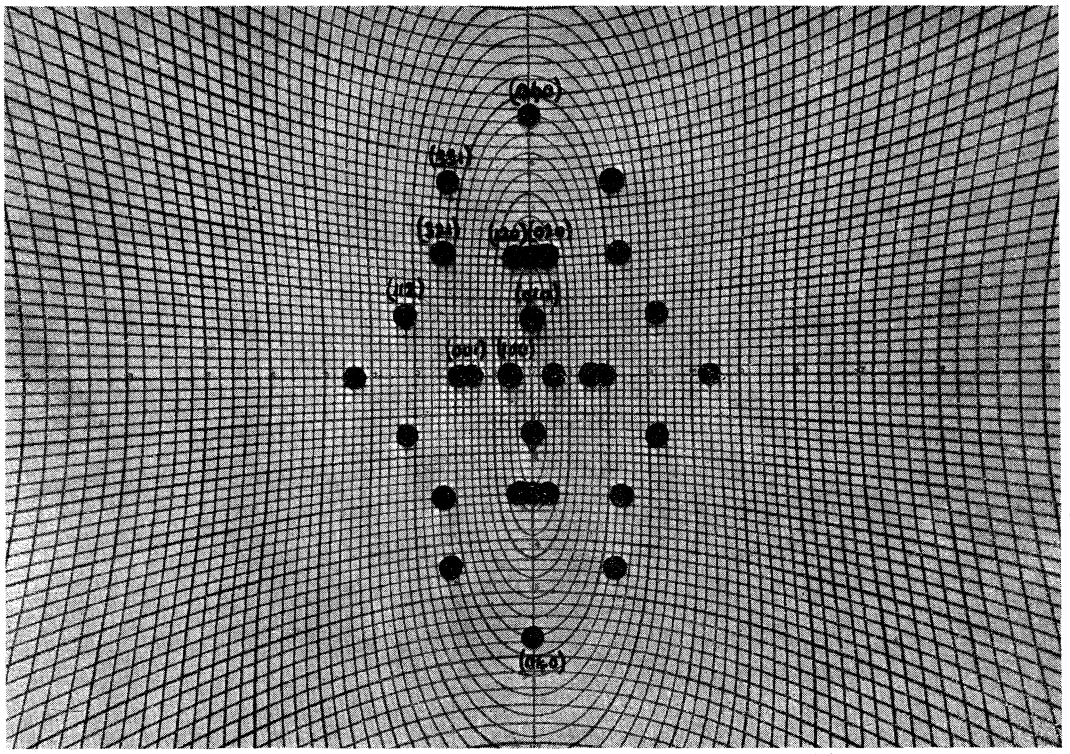


FIG. 1.—Hair. α-form.

be compared with Plate 2, figs. 1, 2, 3, 4, and 5A, which show how in the actual photographs definition is lost by the overlapping and dispersion of the spots. The semi-angle of dispersion is of the order of 10°–15°, that is, the crystallites which give rise to the α-photograph lie with a common crystallographic axis roughly parallel to the axis of the fibre. The length of the primitive translation corresponding to this chief crystallographic axis is at least 10·3 Å.U., but may possibly be a higher multiple of 5·15 Å.U.

* J. D. BERNAL, 'Proc. Roy. Soc.,' A, vol. 113, p. 117 (1926).

than this. There are certain indications in the photographs which hint at a primitive translation perhaps as great as 30·9 Å.U., but for the moment it would not be profitable to discuss them further. An exhaustive study with X-rays of longer wave-length will doubtless decide that point later. Actually, the outstanding reflection on the meridian is the strong arc of spacing 5·15 Å.U. which we have named (020), and which is closely flanked on either side by the reflection (120). The appearance of this lip-shaped trio of overlapping dark arcs is very characteristic of hair photographs. What we may call the " pseudo-primitive translation " parallel to the fibre axis is very definitely 5·15 Å.U., which is precisely the now familiar number which was found for cellulose and is the length of a glucose residue. We shall return to this point later. It will suffice here to state that the unit of pattern repeats itself along the fibre axis in the first instance at intervals of 5·15 Å.U. Though the true period is undoubtedly a multiple of this, it is not at all so well pronounced.

The equator is characterised by three reflections, or rather groups of reflections, the first of which is a small spot close to the centre which we have taken as (100). It does not appear to be dispersed, and must therefore correspond to a plane fairly closely parallel to the fibre axis; but there is a radial spreading which makes it difficult to estimate its true spacing. The mean spacing is about 27 Å.U., but there may be an error of $\pm$ 2 Å.U. in this estimate. The most prominent interference on the equator is the disproportionately large spot formed round (001). There is little doubt that this is not a single reflection. It is spread over about 3 Å.U. and could include (001), (101), (300), and (201). The combined effect of this radial overlapping and a dispersion of some 10° would give rise to the appearance observed. The region of maximum density corresponds to 9·8 Å.U., and as would be expected, the inner edge of the spot is slightly concave. The only other reflections on the equator are located in a vague patch of mean spacing about $3\frac{1}{2}$ Å.U. Of course, there are a number of reflections which could be assigned to this area.

On the first " layer-line," of translation 10·3 Å.U., weak reflections of this spacing may be seen on Plate 2, figs. 1 and 4, while fig. 2 shows in addition diffuse reflections suggestive of the plane (210). Further out lies another diffuse spot which might well be (112), though its position on the first hyperbola is not well defined.

The second layer-line shows the strong arcs from (020) and (120), which are in turn flanked by the horn-shaped reflections from (321); but the sole representatives of the third layer-line are what appears to be a very faint (030) and a pair of faint overlapping arcs which are probably (331). In the region of the fourth layer-line nothing may be discerned but a very weak (040).

Taken as a whole the photograph is what might be expected from an imperfectly crystalline system in which the only sharply defined translation is that which is parallel to the fibre axis; in other words, it suggests long filament-like molecules which cling together sideways with varying degrees of perfection. The radial spreading of (100), and possibly of (001) too, is very marked, and indicates either malformed junctions or

mixed-crystallisation effects. On the other hand, the fact that (100) is the spot most free from dispersion points to an arrangement in which the dispersion is confined to a real or imaginary cylinder, the radii of which are the normals to the planes (100). It is exactly this distribution which has already been found for ramie fibre.*

The reflections described above may be referred to an orthogonal cell of dimensions, $a = 27$ Å.U., $b = 10{\cdot}3$ Å.U., $c = 9{\cdot}8$ Å.U. Table I gives a list of the observed and calculated spacings as derived from a study of the whole of the available material.

TABLE I.—Hair, α-form.

Rectangular cell: $a = 27$ Å.U., $b = 10{\cdot}3$ Å.U., $c = 9{\cdot}8$ Å.U.

Plane.	Observed spacing.	Calculated spacing.	Intensity.
(100)	27	—	Strong.
(001)	9·8	—	Very strong.
(101)	—	9·21	
(300)	—	9·0	
(201)	—	7·93	
(010)	10·3	10·3	Very weak.
(112)	4·5	4·37	Weak and vague.
(020)	5·15	—	Very strong.
(120)	5·05	5·06	
(321)	4·1	4·07	Moderate.
(030)	3·3 ?	3·43	Very weak.
(331)	3·0	3·05	Weak.
(040)	2·6	2·58	Very weak.
(—)	3½	—	Very weak and vague.

There remain two other features of the α-photograph which should be pointed out here. The first is that, commencing quite sharply at a distance from the centre corresponding to just over 5 Å.U., the whole system of spots appears to be overlaid by a broad halo. The lengthy exposure required for good hair photographs is an indication that only a fraction of the hair substance is in a true, or approximately true, crystalline state, and what we know of " amorphous " X-ray halos would lead us to expect a diffuse reflection of the kind observed. Amorphous halos tend to reveal the " most probable " inter- or intra-molecular distances in a non-crystalline system; and the non-crystalline fraction of the hair substance, being built of combinations of α-amino acids which must have certain relatively small spacings in common, would naturally yield such a halo. In addition, the effect will be further enhanced by a certain proportion of matter, in heterogeneous orientation, corresponding to the aligned crystallites which give rise to the α-photograph described above. That there actually is some crystalline protein in random orientation is shown by the fact that in several of the photographs obtained a weak " powder ring " can be traced passing through (001).

* See papers by HERZOG, SPONSLER, MARK and others.

The second of the additional points of interest mentioned above is that, in photographs of the fine animal hairs, such as Merino wool, much of the centre is obscured by another halo of high "spacing." Plate 2, fig. 3, shows this effect well; in fact, in Merino photographs, the (100) spots cannot be observed on this account. The effect is less obvious in Cotswold wool and practically non-existent in human hair and porcupine quill. It seems clear that this intense central halo arises from the scales of the hairs, which are most prominent in Merino wool, less so in Cotswold, and least of all in human hair and porcupine quill. The most beautiful photograph of all was obtained from the tip-end of a porcupine quill, and in this case the scales accounted for a negligible fraction of the bulk of the material irradiated.

A method was devised for stripping human hair of the whole of the cuticle and scales. This was accomplished by making the hair the string of a wire bow, of the 'cello pattern, and drawing it rapidly backwards and forwards through coarsely powdered glass under a slight pressure. The arrangement is shown diagrammatically in fig. 2. The glass is

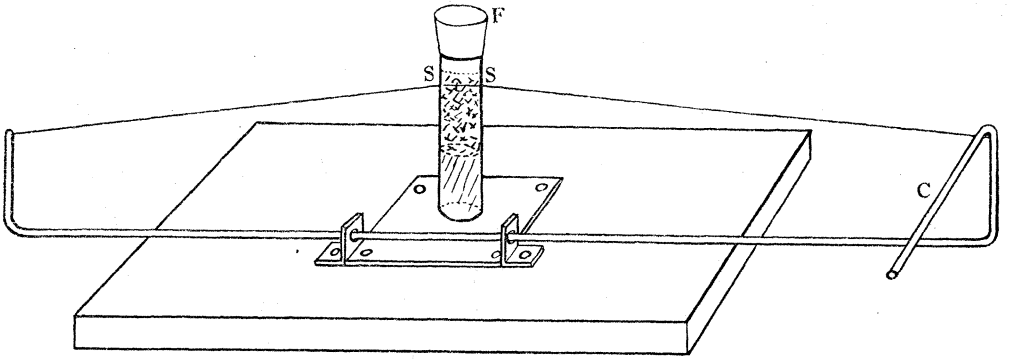


FIG. 2.

moistened with water and kept in movement and under pressure by working the rubber bung, F, while the hair is rapidly drawn through by means of the handle, C. The passage of the hair through the cylinder of powdered glass is permitted by the two fine slits, S, cut in the side of the cylinder. Microscopic examination clearly showed how the scale-bearing protective sheath of the hair is peeled off in long strips by the sharp edges of the broken glass, but on account of the occasional difficulty of seeing the scales on human hair, the descaled fibre was always carefully compared with a piece of the original hair retained for the purpose. The descaling was not considered complete until the peeled fibre, in addition to appearing bare of scales, was both thinner than the original and lighter in colour. Finally, the fibres were soaked in water to allow them to recover from any strains which might have been caused by the previous treatment. Another effective method of peeling the finer fibres, which frequently break in the apparatus just described, is to thread the fibre through a short length of glass capillary tube, mount it taut on the bow, and then to slide the tube along the fibre so that the sharp edge of the glass shaves off the cuticle. The shavings are easily visible and may be collected if necessary.

The X-ray photograph of peeled, unstretched human hair was just the same as that of normal human hair, except that the removal of the scales appeared to bring about an increase of definition. It is shown in Plate 2, fig. 1. This experiment demonstrated that the α-photograph described above arises from the main hair substance of the cortex, to which may be referred the majority, if not all, of the characteristic tensile properties, and justified any subsequent discussion of these properties in the light of X-ray observations. This conclusion was indeed fairly sure from the fact that all fibres examined, in spite of widely differing appearance and dimensions, gave substantially the same X-ray photograph; but the peeling of the fibres by purely mechanical means was necessary to settle all doubts. There then remained only the suggestion that the prominent scales of Merino wool are responsible for the central halo which distinguishes the Merino photograph, but we have not at the moment confirmed this hypothesis on account of the great difficulty of manipulating this fine and crimpy wool.

Another point which might possibly be considered as an objection to the photographs described here is that human hair and prepared wools have been subjected to soap-scouring which might conceivably cause incipient hydrolysis of the protein and thus produce false X-ray effects. That such a criticism is without weight is proved conclusively by the fact that the characteristic features of the α-photograph are independent of whether there is any record of soap-scouring in the history of the fibres examined. For the human hair of fig. 1 soap-scouring must have been very frequent, and it had also formed part of the preparation of the Cotswold wool of Plate 2, fig. 5A. But the fibres used for figs. 2, 3, and 4 had never been in contact with soap of any kind.

With the exception of the porcupine quill, which was photographed in the raw state, all the fibres used in these experiments had been carefully purified of all traces of the natural grease by extraction with ether and alcohol in a Soxhlet apparatus, followed by washing with distilled water.*

The High Tension Photograph.

It is difficult to stretch simultaneously a large number of hairs to an extension of 70 per cent. and yet be sure that no slipping has occurred in the clamps. Human hair is the most troublesome in this respect, because of its small, smoothly-packed scales. Neither a metal clamp nor setting in cement will hold a bundle of hairs for a long time under tension, but a combination of these two methods was found to be effective. The arrangement for winding the hairs in parallel position on the stretching-frame, and the

* Plate 3 shows photo-micrographs of Merino wool and human hair on the same scale. For these beautiful photographs, obtained by a new method, we are indebted to Mr. J. MANBY, of the University of Leeds. (See 'J. Text. Inst.,' T, vol. 21, p. 231 (1930).)

stretching-frame itself, are shown diagrammatically in fig. 3. The parts of the hair bundle which lie in the grooves of the frame were permeated with molten De Khotinsky cement and the clamps screwed down tightly while the cement was still fluid. After trimming off the unnecessary fibres, the stretching-frame was mounted in the X-ray camera so that the bundle of parallel fibres, about 1 mm. diameter and 1 cm. unstretched length, could be inclined with its long axis at any angle to the X-ray beam.

As already mentioned, stretching the hair is accompanied by a progressive fading of the α-interference figure described above. At 20 to 30 per cent. extension, a new set of spots appear and gradually build up a rotation photograph of the β-form. The new interference figure is fairly prominent in Merino wool stretched to 20 per cent., but is

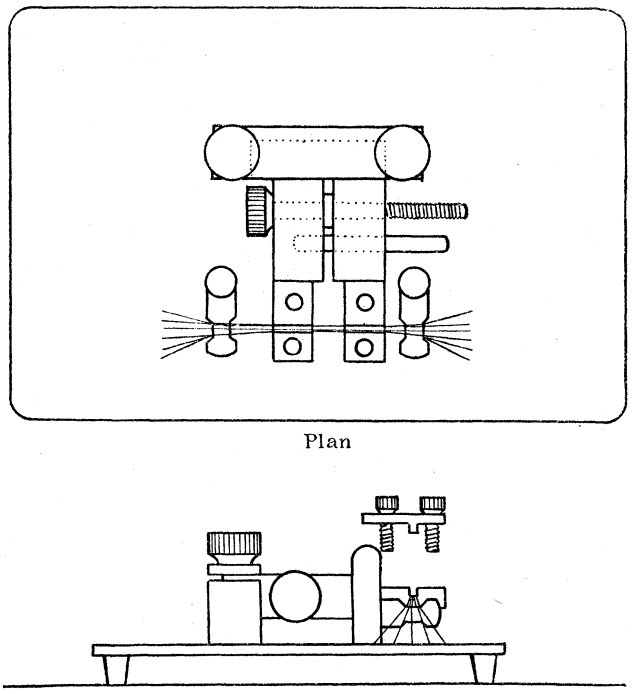


FIG. 3.

not so clear in the case of human hair till about 30 per cent. extension is reached. Plate 2, figs. 5A, 5B, and 5C show successive stages in the transformation of Cotswold wool from the α- to the β-form. It will be noticed that the darkest arcs, (020) and (120), are still present at 35 per cent. extension, though in no photographs are they indubitably present after 60 per cent. extension, even when the fibres are tilted at an angle to the X-ray beam equal to the (020) glancing angle. The large group of reflections located about (001) also fades and finally leaves a smaller spot of spacing approximately that of the original (001). At the same time the (100) near the centre becomes so weak and obscure that it is reasonable to assume that it, too, is destroyed by stretching the fibres, though as a matter of fact in no case was it certain that it had completely disappeared when the fibres broke. The difficulty of settling this point is aggravated by the circumstance that

in photographs of stretched hairs the small-angle scattering appears to be much increased (compare Plate 2, fig. 5c).

Whereas the most prominent layer-line in the α-photograph corresponds to a translation of 5·15 Å.U., the strongest layer-line in the β-photograph gives a translation of 6·64 Å.U., an increase of about 29 per cent. This hyperbola is the one which shows clearly in Plate 2, fig. 5c. The equator is marked by three spots, the (001) mentioned above, a very strong new spot of spacing 4·65 Å.U. which we have called (200), and a very weak (400). On the first hyperbola there is a fairly strong (210), a weaker (111), and a very weak (410). There is no sign of (010), but there is a clear, sharp arc in the position of (020) on the second hyperbola. The fact that this arc never closes up into a sharp spot suggests that it is perhaps in reality composite, for instance, (020) flanked by (120) or (021). On the same hyperbola there is also a faint spot near the position of (220). On the third hyperbola there are weak arcs corresponding to (230), and underneath them a still weaker reflection (030).

All these reflections may be referred to an orthogonal cell of dimensions, $a = 9{\cdot}3$ Å.U., $b = 6{\cdot}64$ Å.U., and $c = 9{\cdot}8$ Å.U. Table II shows the observed and calculated spacings from a review of the whole of the available data.

TABLE II.—Hair, β-form.

Rectangular cell: $a = 9{\cdot}3$ Å.U., $b = 6{\cdot}64$ Å.U., $c = 9{\cdot}8$ Å.U.

Plane.	Observed spacing.	Calculated spacing.	Intensity.
(001)	9·8	—	Very strong.
(200)	4·65	—	Very strong.
(400)	2·4	2·33	Weak.
(111)	4·7	4·73	Moderate.
(210)	3·75	3·81	Strong.
(410)	2·2	2·19	Weak.
(020)	3·32	—	Strong.
(220)	2·7	2·70	Weak.
(030)	2·2	2·21	Weak.
(230)	2·0	2·00	Weak.

Fig. 4 is an ideal diagrammatic representation of the β-photograph plotted on a BERNAL chart. It should be compared with Plate 2, fig. 5c, and with the corresponding diagram for the α-form, fig. 1. The β-photograph is in general better defined than the α-photograph, but it presents the same interesting features which give rise to the impression of long filament-like molecules clinging together sideways with imperfect junctions. Just as in the case of the α-form, most of the spots which should appear are missing; but there is a new departure in the sense that *all but two of the β-spots belong to a single zone* [001]. This strongly suggests that the non-appearance of the theoretical number of reflections is to be ascribed simply to imperfect or variable inter-molecular junctions in

the direction [001]. The sharpness of the reflection (020) indicates that the periodicity along the fibres is as sound as in the α-form, but it would appear that in the β-form there

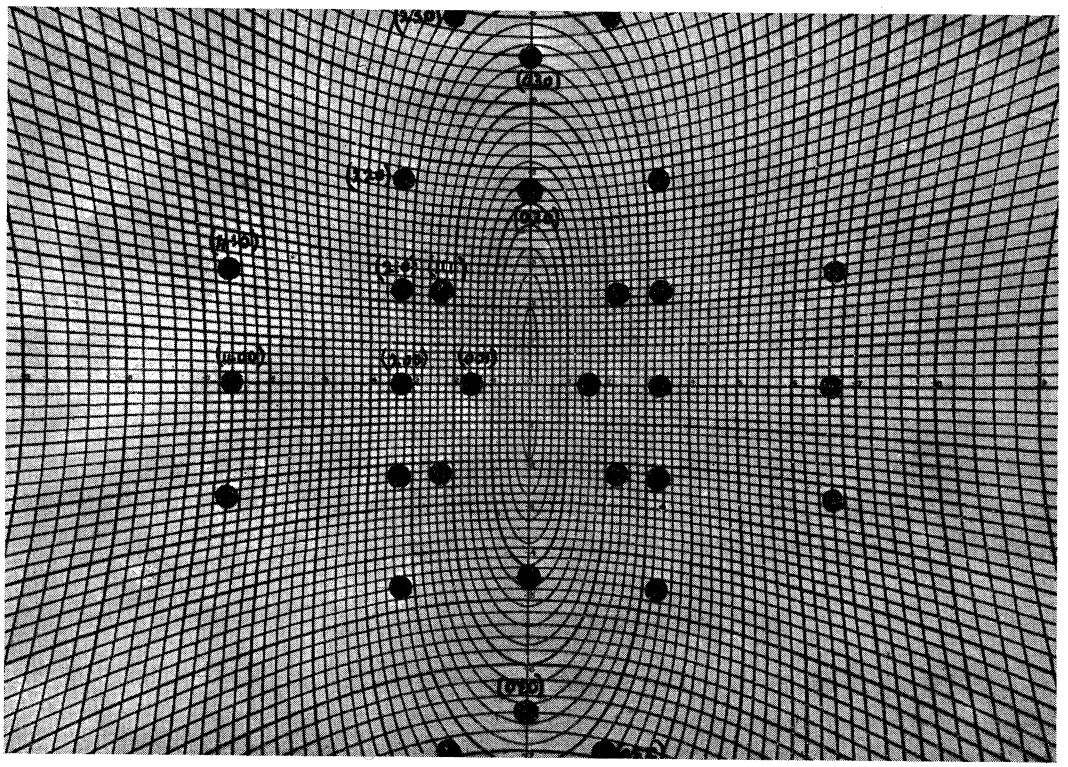


FIG. 4.—Hair, β-form.

is strong inter-molecular cohesion also in the direction [100]. In both cases the reflections other than that arising from the plane at right angles to the fibre length show that diffuseness which would be expected from long thin crystallites lying nearly parallel to the fibre axis.

The Elastic Properties of Hair.

The elastic properties of hair present an exceedingly interesting and complex problem in the physics and chemistry of proteins. The pioneer investigations are those of HARRISON* and SHORTER,† the latter of whom explained the properties then known in terms of the POYNTING and THOMSON‡ "elastische Nachwirkung" model, in which a perfectly elastic system is impeded by a viscous medium. But apparently the first workers to obtain the complete load/extension curve for hair up to the breaking point, and for humidities varying from 0 per cent. to 100 per cent., were KARGER and SCHMID

* 'Proc. Roy. Soc.,' A, vol. 94, p. 460 (1918).

† 'J. Text. Inst.,' T, vol. 15, p. 207 (1924); 'Trans. Far. Soc.,' No. 59 (1924); 'J. Soc. Dyers and Colourists,' vol. 41, p. 212 (1925).

‡ "Properties of Matter," p. 57.

in 1925,* using the fibre extensometer designed by POLANYI.† From 1926 onwards, the most exhaustive and instructive study of the hair load/extension curve, under a wide variety of conditions, is due to SPEAKMAN, whose results we shall draw upon freely, both in this and subsequent communications.

Fig. 5 shows a set of load/extension curves for Cotswold wool, for humidities varying from 0 per cent. to 100 per cent., at a temperature of 25° C. They are due to SPEAKMAN,‡ but have been slightly modified from his original curves, in which the abscissæ

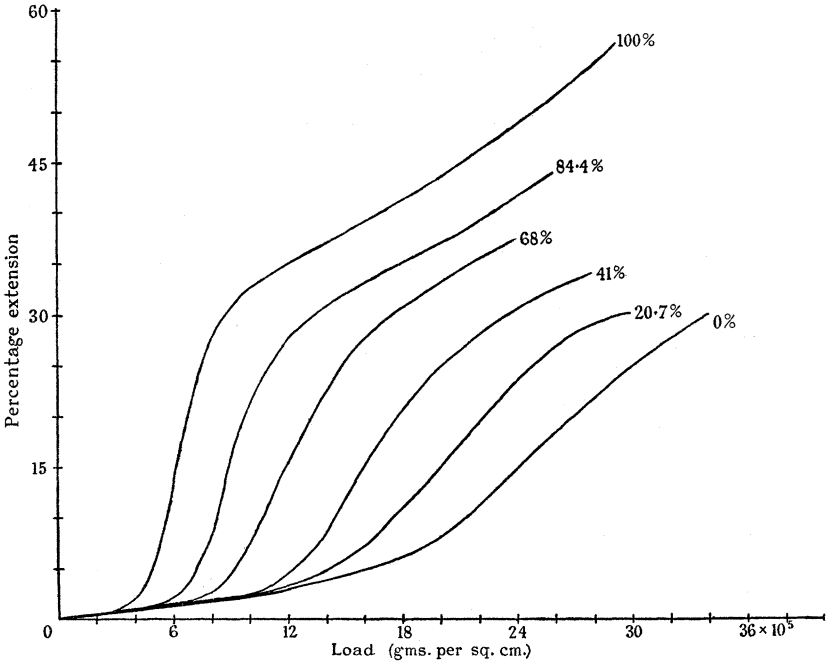


FIG. 5.

are grams per square centimetre *initial* cross-section of fibre. In fig. 5, on the assumption that the fibre density is constant, the original abscissæ have been multiplied by the fibre lengths to give the load in grams per square centimetre of *actual* cross-section. The typical curve is divisible into three main portions : (1) where the rate of extension is slow, HOOKE's law holds, and the elastic behaviour is perfectly reversible ; (2) where the length increases rapidly with little increase of load ; and (3) where there is a return to a slower rate of extension which nevertheless is quicker than the initial rate. The last section of the curve shows in addition another discontinuity, where the rate of extension is once more increased before the fibre breaks. It is important to remember that *the curves shown are for a fairly quick rate of loading*, 1·8 gm. per minute for fibres of diameter about 40 μ.

It is not possible to extend dry hair much beyond 30 per cent. without breaking, for

* ' Z. tech. Physik,' vol. 6, p. 124 (1925).

† ' Z. tech. Physik,' vol. 6, p. 121 (1925).

‡ ' J. Text. Inst.,' T, vol. 18, p. 431 (1927).

which reason, in the extension experiments described here, the fibres were wetted, extended quickly, and then immediately dried. A single exception to this procedure was the case of Cotswold wool extended by 25 per cent. at ordinary laboratory dryness, when the photograph obtained was very much the same as that given by the wool stretched in the wet state to that extension. Such a result might reasonably be inferred from the curves shown, which in reality differ only in the scale of the abscissæ. The presence of water in the fibres at ordinary temperatures simply facilitates the changes that accompany extension. Similarly, though dry hair would probably recover from extension if given sufficient time, the rate of recovery when wet is rapid. *Hair has the striking property of always returning to its original length if wetted after extension.* This is true for extensions even as high as 70 per cent. (1927, *loc. cit.*).

Probably the most remarkable of the elastic properties of hair is that discovered by SPEAKMAN for extensions up to 30 per cent. He showed (1927, *loc. cit.*) that if hair is stretched quickly in water to an extension not exceeding about 30 per cent., then allowed to recover in water for 24 hours, the load/extension curve may be repeated exactly. But *if hair is stretched beyond* 30 *per cent., whether quickly or slowly, the load/extension curve can never be repeated. Less work is required for the second extension.* Fig. 6 shows two successive curves obtained with Cotswold wool for an extension of 50 per cent.

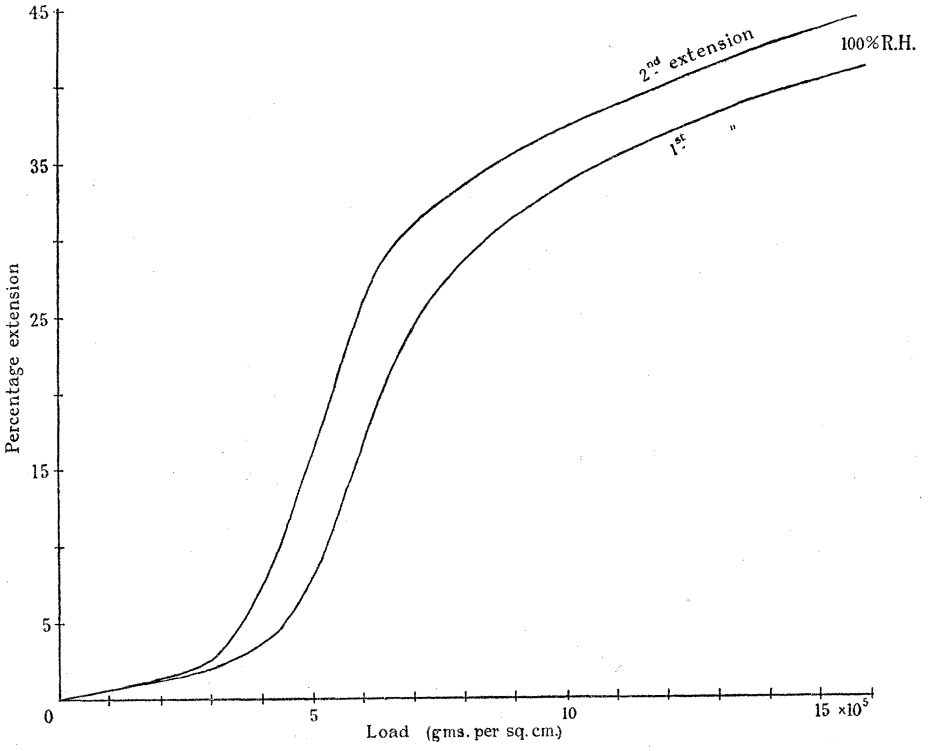


FIG. 6.

SPEAKMAN measured the reduction in energy of extension between successive extensions for a series of increasing extensions, and by extrapolation deduced the point where

this permanent internal breakdown begins. He found 27 per cent. for human hair and 34·5 per cent. for Cotswold wool, with intermediate values for other kinds of wool. But an exact extrapolation is difficult, and it would appear that this yield point is very much the same for all hairs.

SPEAKMAN'S explanation of the load/extension curve of hair is based on an observation of NATHUSIUS,* who showed that the fibre cells can be broken down by prolonged treatment with dilute ammonia at low temperatures, when they are found to consist of long threads or fibrillæ about 1 μ thick.† SPEAKMAN suggested that the steep second part of the curve is due to the rotation of these fibrillæ into alignment, and that the permanent breakdown is due to rupture of fibrillæ when alignment is complete. There are certain difficulties in the way of this theory, one of which is that it would mean that the fibrils of all animal hairs would have approximately the same dispersion, since all the load/extension curves are typically the same. For an extension of 30 per cent. the semi-angle of dispersion, ϕ, assuming that the directions of the fibrils are distributed at random within a cone of this semi-angle and that the thickness of a fibril is small compared with its length, is given by

$$1 \cdot 30 = \phi / \sin \phi,$$

whence $\phi = 70°$. This is greatly in excess of the dispersion of the spots of the α-photograph and of the fibrils which were seen under the microscope in a chemically-treated or diseased human hair; in fact, these fibrils were almost parallel to the fibre axis, and two isolated cortical cells, themselves built up of fibrils, were some three hundred times as long as they were broad.

The results of X-ray analysis offer what appears to be the true explanation of the characteristic elastic properties of hair described above. We know (1) that dry hair will not stretch much beyond 30 per cent. without rupture; (2) that wet hair, if stretched quickly enough and allowed to rest between successive extensions, may be stretched repeatedly up to 30 per cent. without the occurrence of permanent internal breakage; (3) that all the load/extension curves with a quick rate of loading are similar and bend over at about 30 per cent. extension; (4) that the X-ray photographs of unstretched hairs are all similar and are all transformed, on stretching the hairs, into the interference figure of a second phase which first becomes prominent in the region where internal breakage sets in and the load/extension curves turn over; and (5) that the chief translation in the α-photograph of 5·15 Å.U. parallel to the fibre axis gives place to the chief translation of 6·64 Å.U. in the β-photograph, an increase of 29 per cent. Taking the whole of these experimental results into consideration, it seems clear that the course

* 'Archiv. Mikr. Anat.,' vol. 43, p. 148 (1894).

† We were able to perform a similar experiment with human hair which had been stripped of its cuticle, as described above. A descaled fibre was left standing overnight in 10 per cent. aqueous $Na_2S \cdot 9H_2O$, when it was found to be disintegrating into fine threads parallel to the fibre length. The phenomenon is not noticed with normal hair because of the cuticle (see below).

of the typical load/extension curve runs as follows. For about the first 2 per cent. extension the whole system is subject to the control of purely elastic inter- and intra-molecular forces, but at a certain tension some intra-molecular group which is repeated indefinitely along the fibre length at intervals of 5·15 Å.U. yields to the stress and is transformed into another group whose length along the fibre axis is 29 per cent. greater. This phenomenon, acting in conjunction with a certain amount of molecular alignment, gives rise to a sudden rapid increase in the length of the fibre culminating in the crystallisation of a new phase. The shoulder of the curve, the onset of internal breakage, and the appearance of the β-photograph, all mark where the transformation " begins to end " ; that is, where what we may call the " normal molecules "—those straight, unstressed molecular chains which, in series, occupy a length equal to the whole length of the fibre—have completed the transformation and resist further elongation. After this point, there is either a progressive snapping of the transformed molecular chains, or a rupture of the side-junctions between the chains and those parts of the fibre which are capable of still further extension.

It is not proposed to carry out an exhaustive examination of all the elastic properties of hair in this paper. That will be reserved for a later communication, when the elastic properties will be considered in the light of X-ray photographs of hair which has been subject, while under tension, to the action of steam. It will be shown how the action of steam on the β-phase brings about a change which prevents its return to the α-phase and gives rise to the phenomenon known in the textile trade as " permanent set." Furthermore—and this is a striking example of the power of X-ray methods even in such difficult fields as are offered by protein structures—it will be shown how the maximum *true* permanent set which may be deduced from the X-ray data, namely, 29 per cent., is in fact very approximately the same as the highest true permanent set which may be obtained in practice. For the rest, we may say that it is hoped that later X-ray results will explain the nature of the additional mechanism through the agency of which it is possible to extend wet hair at least twice as far as dry hair, and hair in steam at least three times as far as dry hair. At the moment, the only evidence of the action of cold water on the crystallites is afforded by a photograph of Cotswold wool stretched in 5 per cent. stages up to 70 per cent., and left to stand between each stage in a closed vessel over water. The complete extension occupied nearly a fortnight, and at the end the photograph showed unmistakable signs of a spreading of the (111) spot along the first hyperbola, suggesting a disturbance of spacings other than that along the fibre length. But steam brings out this effect very strongly, and it is proposed to discuss it in more detail under that head.

In the presence of water, stretched hair cannot permanently maintain a stress, even at extensions below 30 per cent., and a small load where HOOKE's law fails will in time stretch the fibre as far as 70 per cent. It is for this reason that it is necessary to state whether a given load/extension curve is for a quick rate of loading or not. The *slow* loading curve shows the effect of this plastic flow in that greater extensions are obtained

with given loads (beyond HOOKE's law) than hold in the case of rapid loading, and the shoulder of the curve is raised considerably. Even under constant length, wet, stretched hair gradually loses tension and its power of recovering its original length when the restraint is removed, though it never entirely loses its resilience at ordinary temperatures. The plasticity of wool has been investigated in detail by SPEAKMAN (1927, *loc. cit.*),* who has suggested that it is a property of the fibrillar contents of the cortical cells, while the power of recovery is due to perfectly elastic cell walls.

X-ray examination of the internal rupture and loss of tension under constant length failed to reveal any new diffraction effect. Both in the case of wool and human hair, at 30 per cent. extension and also at 60 per cent. extension, the photographs appeared unchanged after the fibres had stood for 36 hours over water in a closed vessel. The only signs yet detected of the action of cold water are those mentioned above for the case of Cotswold wool at 70 per cent. extension.

One point in the elastic behaviour of hair appears as yet to have received no explanation whatsoever. SPEAKMAN observed (1927, *loc. cit.*) that, in order to be able to repeat the load/extension curve up to 30 per cent., it is necessary (*a*) to stretch the fibre quickly, and (*b*) to allow it to rest unstretched in water between successive extensions. If the precaution (*b*) is not observed, less energy is required for the second extension even though it may be below 30 per cent. It would now appear that the true explanation of this phenomenon is that the relaxation in water is to allow sufficient time for the β-phase to revert completely to the α-phase. When the reversal is complete, the same energy will be required for re-extension.

The Longitudinal Photograph.

As might be inferred from the photographs already described, nothing of further value is given by photographs taken with the X-rays parallel to the fibre length. These showed all the interferences drawn out into DEBYE rings, a result which follows from the dispersion observed in the α-photographs taken with the X-rays perpendicular to the fibre length. Corresponding longitudinal photographs of the β-phase have not as yet been taken.

Chemical.

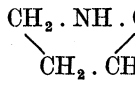
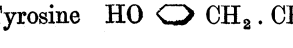
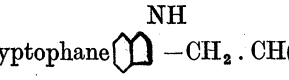
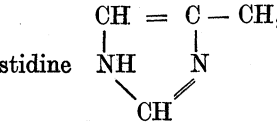
It would not be justifiable at this stage to insist too strongly on the validity of such chemical interpretation as the present X-ray data suggest. Nevertheless, it is true that in a field of the vastness and complexity of protein chemistry, where so much is obscure and yet so full of possibilities, it would be unreasonable to neglect even the faintest hint as to what is the basis of any particular structure type. It is not too much to say that practically nothing illuminating is known of the constitution of the keratins, the proteins from which are built up hair, nails, horn, feathers, etc., and it may well be

* ' Proc. Roy. Soc.,' B, vol. 130, p. 377 (1928).

that the indications of X-ray analysis do actually point the way to a solution, if only we may interpret them correctly. Certainly, there are already a number of striking points which appear to be well worth consideration from a chemical standpoint, and it will perhaps be not out of place to mention them even in this introductory communication.

The most recent list of the hydrolytic products of wool protein* is given in Table III, an analysis which accounts for some 80 per cent. of the wool substance. In addition to this, we know from the work of BARRITT and KING† that the sulphur content of wool is

TABLE III.—Weights of Amino-acids obtained from the Hydrolysis of 100 gm. of Wool.

	gms.
Glycine $NH_2 . CH_2 . COOH$	0·6
Alanine $CH_3 . CH(NH_2) . COOH$	4·4
Valine $CH(CH_3)_2 . CH(NH_2) . COOH$	2·8
Leucine $CH(CH_3)_2 . CH_2 . CH(NH_2) . COOH$	11·5
Serine $HO . CH_2 . CH(NH_2) . COOH$	2·9
Proline 	4·4
Aspartic acid $COOH . CH_2 . CH(NH_2) . COOH$	2·3
Glutamic acid $COOH . CH_2 . CH_2 . CH(NH_2) . COOH$	12·9
Cystine $COOH . CH(NH_2) . CH_2 . S . S . CH_2 . CH(NH_2) . COOH$	13·1
Tyrosine 	4·8
Tryptophane 	1·8
Arginine $C(NH)(NH_2) . NH . CH_2 . CH_2 . CH_2 . CH(NH_2) . COOH$	10·2
Histidine 	6·9
Lysine $NH_2 . CH_2 . CH_2 . CH_2 . CH_2 . CH(NH_2) . COOH$	2·8

by no means constant, even along the length of the same fibre. The percentage of sulphur may vary from 3·03 in coarse medulated Turkey mohair to 5·07 in white dog wool; but it is difficult to assess these results at their true value until information is forthcoming about the accompanying variations in the proportions of the amino-acids

* From "Wool: A Study of the Fibre," by S. G. BARKER. (Publication of the Empire Marketing Board, 1929.)

† Publications Nos. 62 and 113 of the 'Brit. Res. Assoc. for Woollen and Worsted Industries,' 1926 and 1929.

which do not contain sulphur. RIMINGTON* has shown that, with the possible exception of the case of camel hair, the sulphur can all be accounted for as cystine, though in a more recent paper† the same writer has shown that neither free —S—S— nor free —SH linkages are present in undamaged wool.

The Structure of Cystine.—In order to be able to make the fullest possible use of the crystallographic data obtainable from hair protein, some knowledge of the crystal structures of both the amino-acids given in Table III and other related compounds is probably indispensable. One of the most important constituents is undoubtedly cystine, $COOH . CH(NH_2) . CH_2 . S . S . CH_2 . CH(NH_2) . COOH$, since a number of experiments indicate that the elastic properties of hair are intimately bound up with the state of combination of the sulphur atoms. Some observations of this nature will be described later, but in the meantime it is necessary to give an account of a preliminary attack on the structures of those simpler bodies which go to make up the more complex systems of the proteins. We have not yet been able to obtain large crystals of cystine, but a micro-crystalline specimen of pure *l*-cystine gave a remarkably fine powder photograph.‡ The spacings bear out the conclusion which has already been arrived at from an examination with the polarising microscope,§ that cystine is either hexagonal or trigonal. Table IV gives the observed and calculated spacings for a hexagonal lattice of dimensions $a = 9{\cdot}40$ Å.U. and $c = 9{\cdot}42$ Å.U., the indices being referred to three axes only, with $\gamma = 120°$. The intensities were estimated by covering part of the lines with a step-wedge of aluminium foil, 1/1000 inch thick, and making use of the known absorption-coefficient of aluminium for CuKα rays.

The mean density of the powdered cystine, as determined in water in a specific gravity bottle, was 1·65 ; the molecular weight being 240, this value gives three molecules per unit cell. The reflections (00l) are absent unless $l = 3n$, and the space-group,‖ since cystine is optically active, is C_3^2 and C_3^3, or D_3^3 and D_3^5, or D_3^4 and D_3^6, if it is trigonal, but C_6^4 and C_6^5, or D_6^4 and D_6^5, if it is hexagonal. The last-named pair is eliminated, because it involves a molecule symmetrical about three mutually perpendicular dyad axes, which is impossible in this case ; while the first-named pair would make the cystine molecule perfectly asymmetric. It is much more likely that it is symmetrical about a dyad axis, as is required by the remaining three pairs of space-groups. For D_3^3 and D_3^5, and D_3^4 and D_3^6, this dyad axis is perpendicular to the triad axis ; in C_6^4 and C_6^5, it is parallel to the hexad axis. It is not possible from the available data to make an unequivocal choice between these two possibilities, especially as the a and c axes are practically equal in length. It must suffice at the moment to state that the

* ' Biochem. J.,' vol. 23, pp. 41 and 726 (1929).

† ' Biochem. J.,' vol. 24, p. 205 (1930).

‡ Supplement to ' Nature,' March 1, 1930, p. 318.

§ P. GROTH, " Chemische Kristallographie," vol. 3, p. 209.

‖ W. T. ASTBURY and K. YARDLEY, ' Phil. Trans.,' A, vol. 224, p. 221 (1924).

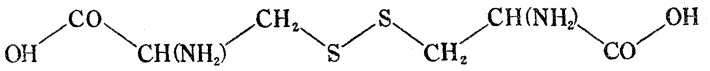
crystal structure of cystine is based on a threefold screw of molecules which are each probably symmetrical about a dyad axis.

TABLE IV.—Cystine, $COOH . CH(NH_2) . CH_2 . S . S . CH_2 . CH(NH_2) . COOH$. Hexagonal lattice, $a = 9{\cdot}40$ Å.U., $c = 9{\cdot}42$ Å.U. Density $= 1{\cdot}65$. Three molecules per cell. Absent reflections, $(00l)$ unless $l = 3n$. Space-group, C_3^2 and C_3^3, or D_3^3 and D_3^5, or D_3^4 and D_3^6, or C_6^4 and C_6^5, or D_6^4 and D_6^5.

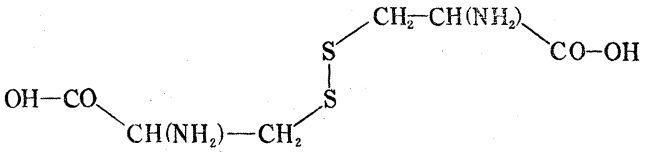
Plane.	Observed spacing.	Calculated spacing.	Intensity.
$(1\bar{2}0)$	4·70	4·70	100
(200)	4·15	4·07	20
(111)	—	4·21	—
(003)	3·14	3·14	50
$(1\bar{3}0)$	—	3·08	—
(120)	—	—	—
$(2\bar{2}2)$	—	—	—
(300)	2·72	2·71	35
$(11\bar{3})$	—	2·78	—
$(1\bar{2}3)$	2·59	2·61	15
(113)	—	—	—
$(2\bar{4}0)$	2·33	2·35	15
(222)	2·15	2·11	12
(130)	—	2·26	—
$(1\bar{4}0)$	—	—	—
$(3\bar{3}3)$	2·04	2·05	8
$(2\bar{4}6)$	—	—	—
(121)	1·95	1·95	12
(140)	1·77	1·77	12
(500)	1·68	1·63	5
$(4\bar{4}4)$	1·56	1·54	5
(240)	—	—	—
(006)	—	1·57	—

That the crystals, as seen under the microscope, are thin hexagonal plates suggests a basal cleavage with little or no molecular overlapping in the screw. As a matter of fact, such an arrangement would explain, too, the main features of the powder photograph, such as the absence of (100) and the great intensity of $(1\bar{2}0)$. It would involve a molecule lying in the basal plane, symmetrical or pseudo-symmetrical about a dyad axis, and with a thickness of 3·14 Å.U. (the spacing of (003)) and an overall length probably equal to that of the a-axis, 9·4 Å.U.

The dimensions of the unit cell make it improbable that the cystine molecule is of the form



but rather something of the form



The length of this latter system would be practically the same as that of the *a*-axis (9·4 Å.U.), whereas the former would be much too long.

The Action of Sodium Sulphide.—Knowing as we do that undamaged wool does not give the reactions of —S—S— and —SH, it is perhaps not surprising that unstretched wool and hair do not betray any of what we may call the " free spacings " of cystine. On the other hand, it is known—and this investigation has in a number of ways confirmed the fact and supplied the explanation—that *stretched hair is more vulnerable to the action of reagents than unstretched hair.* We are thus permitted to ask ourselves whether it is not indeed much more than a coincidence that *the most intense X-ray reflection given by stretched hair has the same spacing as the most intense reflection given by cystine.* In the β-form of hair it is (200), spacing 4·65 Å.U., and in cystine ($1\bar{2}0$), spacing 4·70 Å.U. In both cases this spacing is at right angles to the chief crystallographic axis, and is actually what we have postulated above to be the half length of the cystine molecule and the full length of the cysteine molecule, SH . CH_2 . $CH(NH_2)$. COOH.

Among the most powerful solvents of hair are the alkali sulphides, and it has been established for some time that the reaction is accompanied by the liberation of both free —S—S— and free —SH linkages. The exact nature of the interaction between keratin and sodium sulphide is unknown, but in the course of these X-ray experiments we have made some observations which may possibly throw light on what is happening. They show that stretched hair is far more susceptible to the sulphide action than is unstretched hair. While in the latter case there is a continuous destruction of the protein, *the reaction with stretched hair takes place in two stages. There is an immediate non-solvent reaction followed by a continuous destructive solvent action which is, however, more rapid than in the case of unstretched hair.*

Plate 2, figs. 6A and 6B are photographs of human hair stretched to 30 per cent. and tilted at $13\frac{1}{2}°$ to the X-ray beam in order to show up clearly the reflection (020). For fig. 6A the hair had simply been stretched in water and dried immediately. It will be noticed that the β-phase is just beginning to appear. After the same stretched and dried hair had been immersed for 8 minutes in a 1 per cent. aqueous solution of Na_2S . $9H_2O$, then washed for half an hour with water and finally dried, the photograph shown in

fig. 6B was obtained. It shows a remarkable increase in the development of the β-phase.* Further trials proved that the effect may be observed after even shorter times of immersion—in fact, it seems clear that it is delayed no longer than the time required by the solution to penetrate the fibres, and once it is developed, the immersion may be prolonged to 20 minutes without further change in the photographs.

That this effect is to be ascribed definitely to the action of sodium sulphide and not to that of caustic soda produced by hydrolysis of the sulphide, is shown by the fact that on repeating the test with a chemically equivalent strength of caustic soda (1/3 per cent.), no appreciable change in the photographs was observed after 10 minutes' treatment.

A further series of similar experiments was made with Cotswold wool kept stretched at 70 per cent. extension. At this extension the β-photograph is already practically at its best, and the initial effect of Na_2S solution shows itself more as a clarifying action than as an actual increase of the β-phase. In particular, *the* (200) *spot, of spacing* 4·65 *Å.U., becomes very clear and intense.* A photograph taken after 50 minutes immersion (followed, as in all the experiments described in this section, by washing and drying) showed the onset of a second effect, in which the β-phase was apparently returning once more to the α-state, but this time to an α-state considerably dispersed, as evidenced by the re-appearance of (020) and the drawing out of (001) into a pronounced arc. An additional immersion of 1 hour's duration produced little further change. The wool was then placed in water to allow it to recover its original length, a process which occupied three days, as opposed to the half-hour or so which would be required by normal, untreated wool. A final photograph of the fibres in the relaxed state showed what appeared to be the α-phase almost completely dispersed into continuous DEBYE rings.

In order to convey a more complete impression of the changes just described, it must be added that they are accompanied by progressive destruction of the wool protein and by characteristic swelling phenomena of a magnitude depending on the strength of the sulphide solution and the time of immersion. At the end of the experiments with Cotswold wool the fibre bundle had shrunk to only a fraction of its initial size, yet had the power of swelling enormously in the sulphide solution; and though the lateral swelling amounted to perhaps 500 per cent., it was still further increased on transferring the fibres from the solution to pure water, a fact which seems to indicate that in its later stages the process is more or less of an osmotic nature. As would be expected, the swelling power is largely lost on drying after washing out the sodium sulphide.†

Hair saturated with Na_2S solution exhibits a jelly-like appearance, and its resistance to extension is enormously decreased. A third series of experiments was carried out

* There is evidence, which will be given later, that Plate 2, fig. 6B is perhaps not strictly a photograph of the β-phase, but of a derivative which gives an almost identical interference figure.

† It is fascinating to watch the changes undergone by a hedgehog spine immersed in a 10 per cent. solution of $Na_2S \cdot 9H_2O$. It will increase its length by some 50 per cent. and its thickness by several times; but on washing and drying it is left as a small, shrivelled husk.

as an attempt to align the keratin crystallites by slow stretching of the fibre while in this gelatinous state. Human hair was allowed to extend in a 1 per cent. solution under a small weight of about 1 gm. per fibre until the fibre length was doubled, after which it was washed and dried at the extended length. But the photograph failed to reveal anything of additional value. It seemed to represent the α-phase in incompletely random orientation—something between the photograph of Cotswold wool after 2 hours' treatment at 70 per cent. extension and that of the same wool after return to its original length. Fortunately, however, this failure was in part compensated by another interesting observation, that as the fibre was slowly pulled out in the solution, flocculent decomposition products oozed out from its interior. This at once suggested further microscopic examination, with the result that it was shown that even after prolonged treatment with dilute sodium sulphide solution the scale-sheath of the fibre remains unattacked. On the other hand, the swelling accompanying the reaction in the cortex can produce such an internal pressure that the scale-sheath is split from end to end, the final appearance of the fibre then resembling that of a crushed, over-ripe banana. It is instructive to note that not only the cortex, but also the scale-sheath, has a tendency to split *longitudinally*.

The speed of the reaction between Na_2S and unstretched human hair is of a different order from those described above, since an immersion of 2 hours in a 1 per cent. solution of $Na_2S \cdot 9H_2O$ resulted in little or no change in the α-photograph. On continuing the treatment, photographs taken at various intervals up to 22 hours showed a gradual loss of orientation in the crystallites, but the disarrangement was by no means complete at the end of this period. It was, however, observed that the commencement of the change in the α-photograph was marked by the onset, after $2\frac{3}{4}$ hours' immersion, of a new swelling phenomenon through which the *length* of the fibres increased by as much as 50 per cent. without the application of external tension (see note above on hedgehog spines). On transferring the fibres from the solution to pure water, the longitudinal swelling subsided and was replaced by an increased lateral swelling.

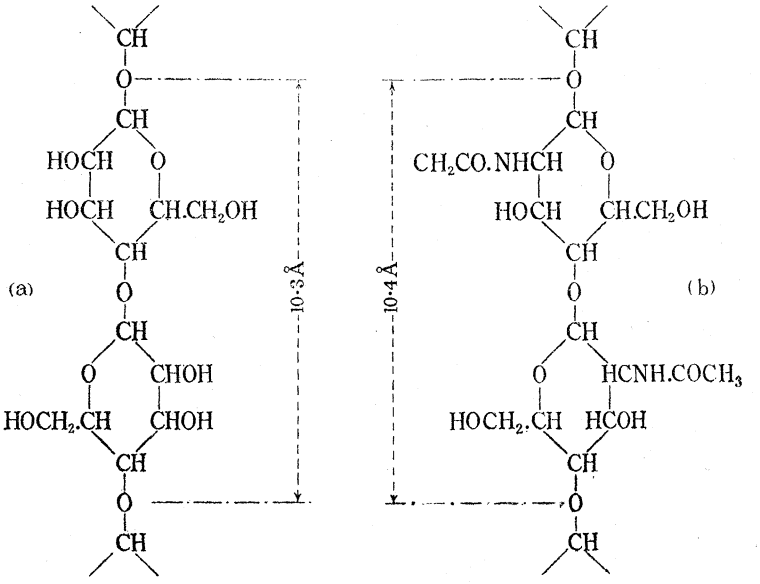
It is obvious, if only from these brief notes, that the problem of the interaction of Na_2S and the keratins is one of extraordinary interest and no little complexity; in fact, one may safely say that it is the problem of the structure of the keratins themselves. It would be indefensible at this stage to rush to hasty conclusions, but it is hard to resist the suggestion that the liberation by Na_2S of free —S—S— and —SH, the sudden intensification by the same reagent of the β-phase or of some close derivative, the similarity in spacing and intensity between the chief reflection of cystine and that of the β-phase, and the crystallographic deduction that this spacing is very likely the half-length of the cystine molecule, are all aspects of one and the same structural feature, that *in the β-form of the keratins there are molecular chains linked side-to-side by molecules of cystine or cysteine.*

In the later stages of the reaction between stretched hair and sodium sulphide it would seem that the molecular chains, themselves, are also ruptured, with the

consequence that some of the β-phase, relieved of tension, reverts once more to the α-phase; but because there has been such a destruction of protein in the body of the fibre, the original alignment of the crystallites is lost.

The Keratin Chain.—The combined evidence of chemical and X-ray analysis, when brought to bear on the problem of fibre structure in both organic and inorganic fields, is undoubtedly leading to a relatively simple generalisation, in fact, to a conclusion no more profound than that fibres are what they are because their inner molecular structure is also of a fibrous nature. In only a few years the literature of the subject has grown too great to permit detailed reference here, and the reader should consult the writings of MARK, MEYER, HERZOG, SPONSLER, HESS, HAWORTH, STAUDINGER, and many others, if a thorough account is required of the work that has been carried out on the structure of cellulose, fibroin, chitin, etc. The properties of hair and the type of the X-ray photographs which have been described above do not offer us any sufficient reason to doubt that the animal fibres so far examined must possess certain fundamental features analogous to those of the vegetable fibres discussed elsewhere. Whatever may be the constitution of the keratins as a class, we are justified by the experimental results now before us in assuming as a sound working hypothesis that keratin fibres, like cellulose fibres, owe many of their properties to the repetition along the fibre of comparatively simple units to form molecular chains.

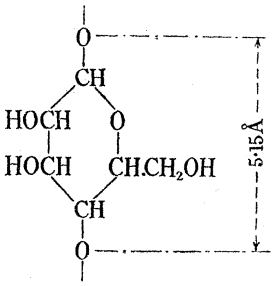
The molecular chains of cellulose and chitin* are believed to be based on the formulæ (*a*) and (*b*), respectively. But we have an additional purpose in quoting these two particular chains, and that is, to draw attention to the fact that, in both, the length of the



repeating pattern is very approximately the same as that found in the α-photograph of hair, viz., 10·3 Å.U. Actually, in both cellulose and hair, the most important

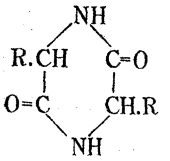
* K. H. MEYER, 'Z. angew. Chem.,' vol. 34, p. 1 (1928).

repetition along the fibre axis—what we have called above the " pseudo-translation "—is 5·15 Å.U., a length which is now recognised as that of a glucose residue, a hexagonal ring built up of five carbon atoms and an oxygen atom, with another oxygen atom acting as a " bridge " to the next hexagonal ring, thus :—



We wish to suggest here that *the basis of the unstretched fibrous keratins is a series of hexagonal ring systems linked along the fibre axis by " bridge atoms,"* in a manner analogous to what is generally accepted for the cellulose and related structures. In point of fact, there is a considerable body of evidence in favour of such a hypothesis. The keratins are remarkably resistant to chemical reagents, and they are not attacked by pepsin, trypsin, or bacterial tryptases. An open peptide chain seems quite out of the question in the α-form of hair. In the words of a recent text-book,* " their resistance to decomposition and to digestion by enzymes suggests that there must be special structural linkages in the keratin molecule." Whatever the detailed nature of these special structural linkages, it is now proposed that they must conform to the general outlines described above.

A familiar hexagonal ring system, the existence of which in intact proteins has been demonstrated by ABDERHALDEN and KOMM,† is the 2 : 5 diketopiperazine ring :—

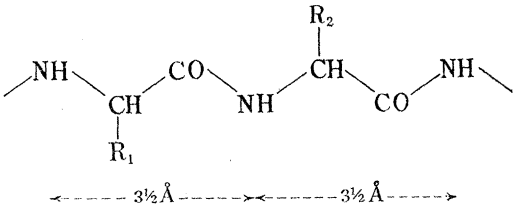


But a ring in itself is too short to account for the whole of the 5·15 Å.U. ; in addition, some kind of ring-to-ring bridge atom must be postulated in order to complete the required length. On the other hand, the diketopiperazine ring does possess a structural feature which seems to be shown also by the repeating ring system proposed here for the keratins. The diketo-ring is formed by the condensation of *two* amino-acids ; and if it is true that the transformation from the α- to the β-form of hair is accompanied by a destruction of the ring system (5·15 Å.U.) to produce a longer, more reactive system (6·64 Å.U.), then certainly the stretched structure is characterised by a strong

* D. JORDAN LLOYD, " The Chemistry of the Proteins."

† ' Z. Physiol. Chem.,' vol. 139, p. 181 (1924).

X-ray reflection, not of spacing 6·64 Å.U., but of spacing 3·32 Å.U., a fact which suggests that the elongated molecule is in some way of a two-fold nature, in the sense that it consists of two similar parts attached end to end. In this connection it may be mentioned that the ordinary peptide chain



may be considered to be built up of similar sections each of length equal to about $3\frac{1}{2}$ Å.U., which is a little larger than the spacing, 3·32 Å.U., found in β-hair. In view of the fact that a spacing does not necessarily equal a chief intra-molecular distance, it is possible that the spacing, 3·32 Å.U., may be evidence of the existence of peptide chain in β-hair. MEYER and MARK* have already put forward this simple arrangement as the structural basis of silk fibroin, in spite of the fact that silk, though free from sulphur, from certain points of view may be classed as a keratin (*loc. cit.*).

The Contents of the Unit Cell.—From the evidence as yet available, we cannot fix the dimensions of the unit cell of either α- or β-hair with any degree of finality. We may only suggest those of a cell which represents to a first degree of approximation the repeating characteristics of the structure without actually being the strict unit of pattern. Such a cell, in the low-tension form of hair, appears to be defined by a length of 5·15 Å.U. along the fibre axis, and two lengths of 27 Å.U. and 9·8 Å.U. at right angles to the fibre axis and to each other. There is not the least doubt that the true minimum unit of pattern is greater than these magnitudes imply; still, the smaller unit is repeated approximately within the larger and must be the expression of some chemical grouping which is the structural basis of the completed protein molecule. Similarly, in the β-form, the X-ray diffraction figure focuses our attention on a pseudo-unit defined by a translation 6·64 Å.U. along the fibre axis, and translations 9·3 Å.U. and 9·8 Å.U. at right angles to the fibre axis and to each other.

If we are justified in attaching any significance to these dimensions, then it ought to be possible to link them up with the reversible transformation which exists between the α- and β-forms. Assuming that the density of stretched hair is not very different from that of unstretched hair, then the volumes of the two pseudo-cells should be the same. As a matter of fact, if the spot of spacing 4·65 Å.U. which we have chosen as (200) of the β-form be taken, instead, as (400), this relation is indeed roughly true; for

$$\frac{18{\cdot}6 \times 9{\cdot}8 \times 6{\cdot}64}{9{\cdot}8 \times 5{\cdot}15} \simeq 24,$$

* 'Ber. Deuts. Chem. Ges.,' vol. 61, p. 1932 (1928).

which is sufficiently near to the 27 Å.U. mentioned above, when it is recalled that the spot of this estimated spacing is in reality spread over several Ångstrom units and is too near the central spot to be measured with accuracy.

Let us take, then, the volume of the primary chemical grouping as represented by $9{\cdot}3 \times 6{\cdot}64 \times 9{\cdot}8$ Å.U.^{3}. The density of wool as a whole is $1{\cdot}3$*; and assuming, for want of data, what is probably correct enough for our purpose, that this figure may be applied to the crystalline constituents which have given rise to the X-ray photographs, the "molecular weight" of the primary grouping is $9{\cdot}3 \times 6{\cdot}64 \times 9{\cdot}8 \times 1{\cdot}3 \div 1{\cdot}65 = 477$.

Now it is known that the proportions of free —COOH and free —NH_2 groups in wool are very small, so that in considering the mass-contribution of any of the amino-acids given in Table III, it is necessary to allow for —CO— and —NH— only. Thus the effective molecular weights of the four chief constituents of wool, leucine, glutamic acid, cystine (or cysteine), and arginine, are 113, 112, 204 (or 103), and 155, respectively.

Again we may ask ourselves, is it not something more than a coincidence that the combined weights of leucine, glutamic acid, cysteine, and arginine are practically equal to the weight of the primary molecular grouping which is deducible from the X-ray observations? The equation

$$113 + 112 + 103 + 155 = 483$$

appears to assume a definite significance in the light of the value, 477, found above. It may be objected that the results of hydrolysis are not in equimolecular proportions for the four constituents mentioned (the actual molecular ratios for the quantities given in Table III are $1 : 1 : 1{\cdot}2 : 0{\cdot}7$), but such an argument cannot be taken seriously so long as at least one-fifth of the wool substance remains unaccounted for, and complete analyses are non-existent for the separate components of the wool structure.

Summary.

(1) An X-ray examination has been carried out of Geelong 80's Merino wool, Australian 64's Merino wool, English Cotswold wool, human hair, llama hair, hedgehog spines, and porcupine quills. Apparently, all animal hairs give rise to substantially the same X-ray photograph.

(2) The photograph (α) of unstretched hair is a typical "fibre photograph" and may be referred provisionally to a rectangular cell of dimensions, $a = 27$ Å.U., $b = 10{\cdot}3$ Å.U., and $c = 9{\cdot}8$ Å.U.

(3) On stretching hair, the α-photograph gradually disappears and is replaced by another "fibre photograph" (β), which first becomes prominent at about 30 per cent. extension. The β-photograph may be referred provisionally to a rectangular cell of dimensions, $a = 9{\cdot}3$ Å.U., $b = 6{\cdot}64$ Å.U., and $c = 9{\cdot}8$ Å.U.

* A. T. King, 'J. Text. Inst.,' T, vol. 17, p. 53 (1926).

(4) The α-β transformation is reversible and appears to be based on the elongation of an intramolecular group of length 5·15 Å.U. to another group of length 6·64 Å.U., an increase of 29 per cent.*

(5) The reversible α-β transformation gives a qualitative and quantitative explanation of a number of characteristic tensile properties of hair.

(6) A preliminary X-ray examination has been made of the structure of cystine. The lattice is hexagonal, with three molecules per cell, and $a = 9{\cdot}40$ Å.U., $c = 9{\cdot}42$ Å.U.

(7) X-ray micro-analytical experiments have shown that stretched hair (β-form) is more vulnerable than unstretched hair (α-form); and among other things, that in the case of β-hair the main destructive action of Na_2S is preceded by a rapid non-solvent reaction.

(8) The structure of cystine and the action of Na_2S on the β-form suggest that the latter is based on molecular chains linked side-to-side by nuclei of cystine or cysteine.

(9) The chief molecular grouping of the α-form repeats along the fibre axis with a period equal to the most prominent period of cellulose (5·15 Å.U.).

(10) The whole series of experiments convey the impression of long filament-like molecules which in some way involve the continuous repetition of hexagonal ring systems connected by bridge atoms.

(11) The X-ray measurements suggest that the primary molecular grouping of hair keratin is based on equimolecular proportions of the four chief constituent amino-acids, leucine, glutamic acid, cysteine, and arginine.

The authors wish to express their thanks to Mr. J. B. SPEAKMAN for the loan of specimens of wool and human hair used in his own experiments, and for much valuable information on the physico-chemical properties of these fibres. They are indebted also to the Director and Dr. C. RIMINGTON of the British Research Association for the Woollen and Worsted Industries for a specimen of powdered *l*-cystine.

The expenses of this research are being defrayed by a grant from the Worshipful Company of Clothworkers, supplemented by a grant from the Government Grant Committee of the Royal Society. To both these bodies the authors wish to acknowledge their deep indebtedness.

* [*Note added January 29th*, 1931.—Since communicating the preliminary results outlined in the present paper, we have carried out a further extensive examination of the elastic properties of hair, particularly in relation to the influence of steam, with a view to publication in detail in the second paper of this series. A notice of the conclusions arrived at will be found in "Nature" (W. T. ASTBURY and H. J. WOODS, Vol. 126, p. 913 (1930)), but it seems expedient to mention them here also, because of the bearing they have on certain of the arguments presented above. We have been able to show that by suitable treatment with steam the load/extension curve of hair may be permanently smoothed out, and that elasticity of form may be demonstrated *in cold water* over a

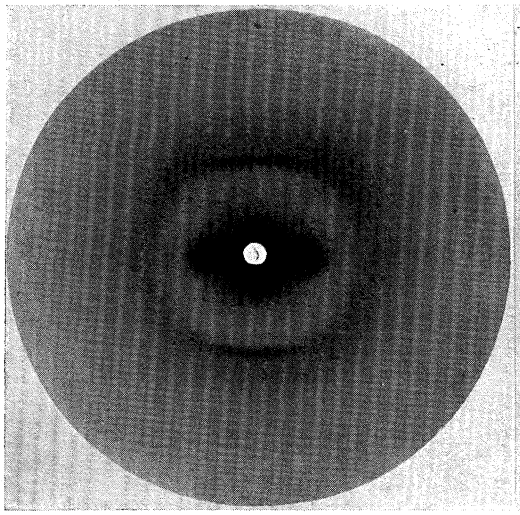


FIG. 1.—Descaled human hair.

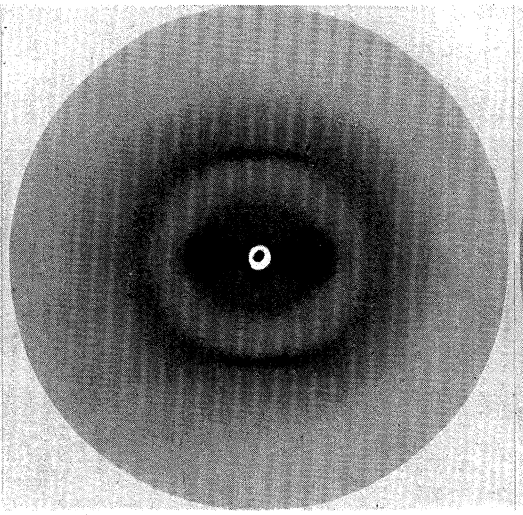


FIG. 2.—Tip end of porcupine quill. $d = 4{\cdot}5$ cm. CuKα.

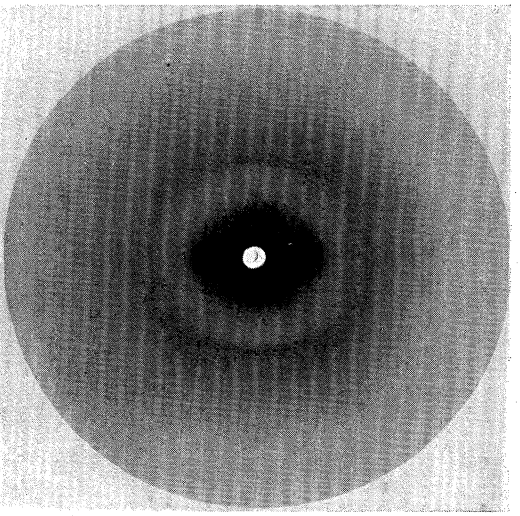


FIG. 3.—Australian 64's merino wool.

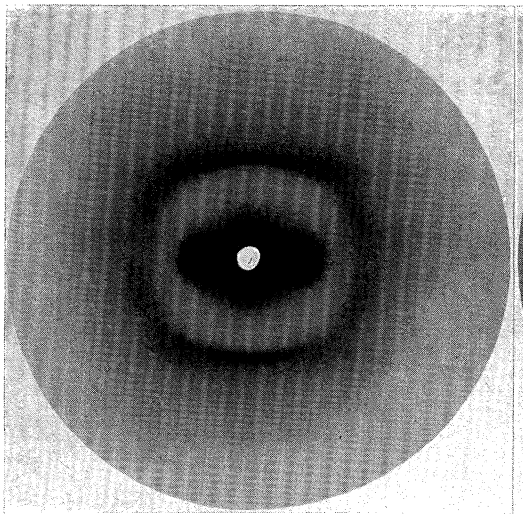


FIG. 4.—English Cotswold wool, free from soap-scouring.

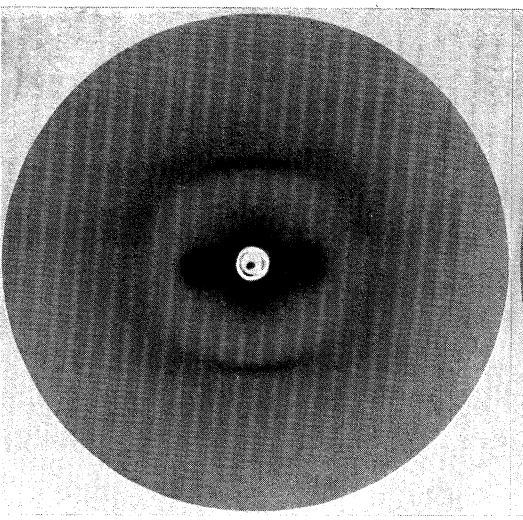


FIG. 5A.—English Cotswold wool, soap-scoured. 0 per cent. extension.

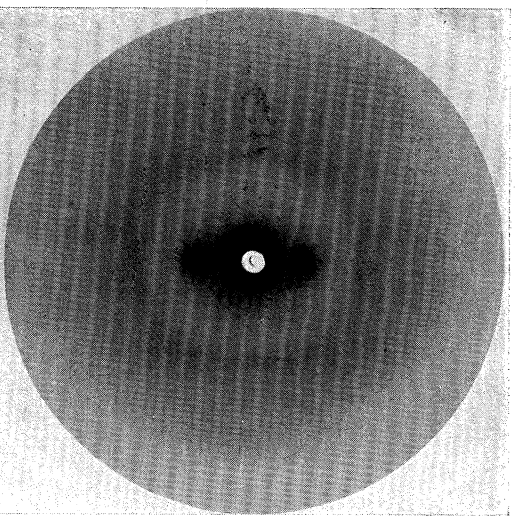


FIG. 5B.—English Cotswold wool, soap-scoured. 35 per cent. extension.

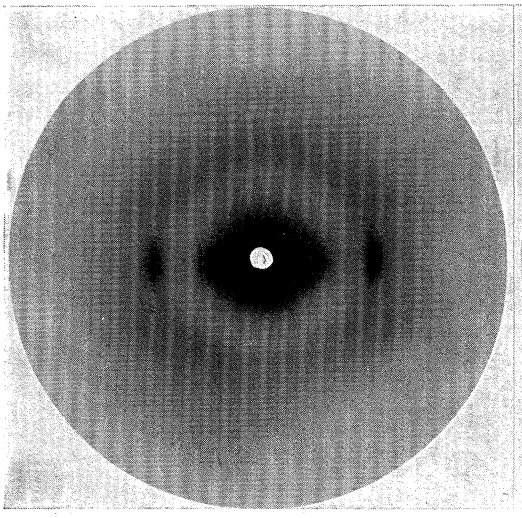


FIG. 5C.—English Cotswold wool, soap-scoured. 70 per cent. extension.

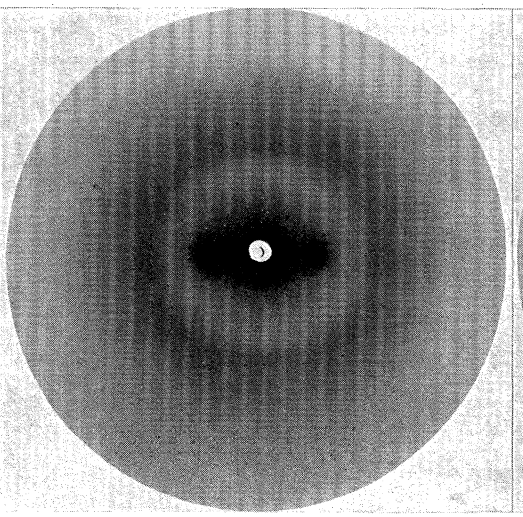


FIG. 6A.—Human hair, at $13\frac{1}{2}°$ to X-ray beam. 30 per cent. extension.

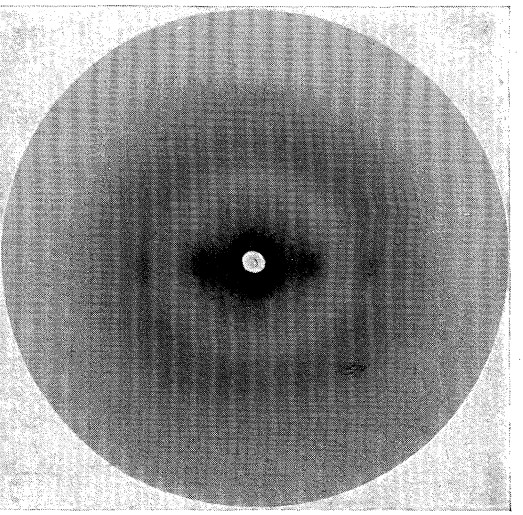
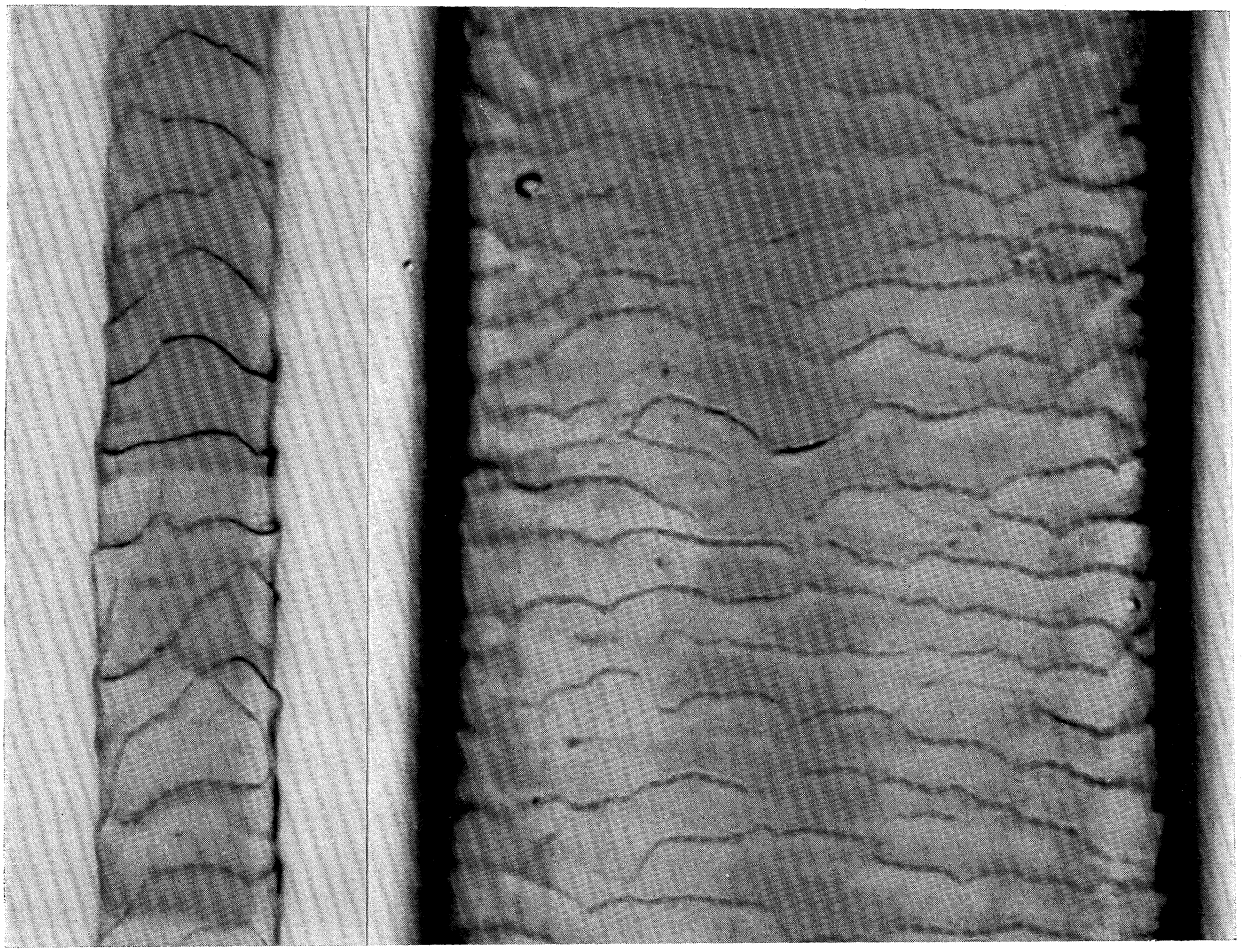


FIG. 6B.—The same as 6A; after 8 minutes immersion in 1 per cent. solution of $Na_2S, 9H_2O$.



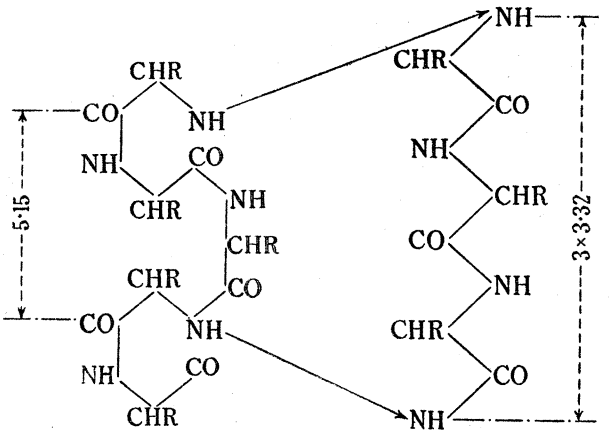
Merino wool fibre
(× 1000).

Human hair
(× 1000).

range of extensions from about −30 per cent. to about +100 per cent. The whole fibre then behaves as an elastic chain whose length may be almost exactly doubled without rupture occurring. Without entering into detailed discussion, we may say that this observation suggests strongly that the *full* $\alpha - \beta$ transformation of hair is accompanied by an elongation of the keratin complex of approximately 100 per cent., and that some relation on this basis must exist between the respective dimensions and features of the α and β X-ray photographs. If now we assume that the two strong meridian reflections, 5.15 Å.U. and 3.32 Å.U., that characterise the reversible transformation, are linked by the relation

$$5.15 \rightleftarrows (3 \times 3.32)$$

we have at once a quantitative explanation of the maximum extension *and also the clue to the nature of the keratin chain.* According to this scheme the transformation may be represented as follows :—



The complete passage from the α-form to the β-form must take place in three stages, corresponding to the fact that hair in cold water may be stretched twice as far, and hair in steam three times as far, as hair which is perfectly dry. It is possible that these three stages are an expression of the three obvious ways in which the α-chain may be written down, but in any case it seems clear that the constituent involved in the middle stage, from about 30 per cent. extension to about 70 per cent. extension, is that part of the hair substance which is sufficiently crystalline to give rise to the X-ray photographs. It is proposed to deal with this, and all the other many points bearing on the complex elastic properties of hair, in the next communication of this series.—W. T. A.]

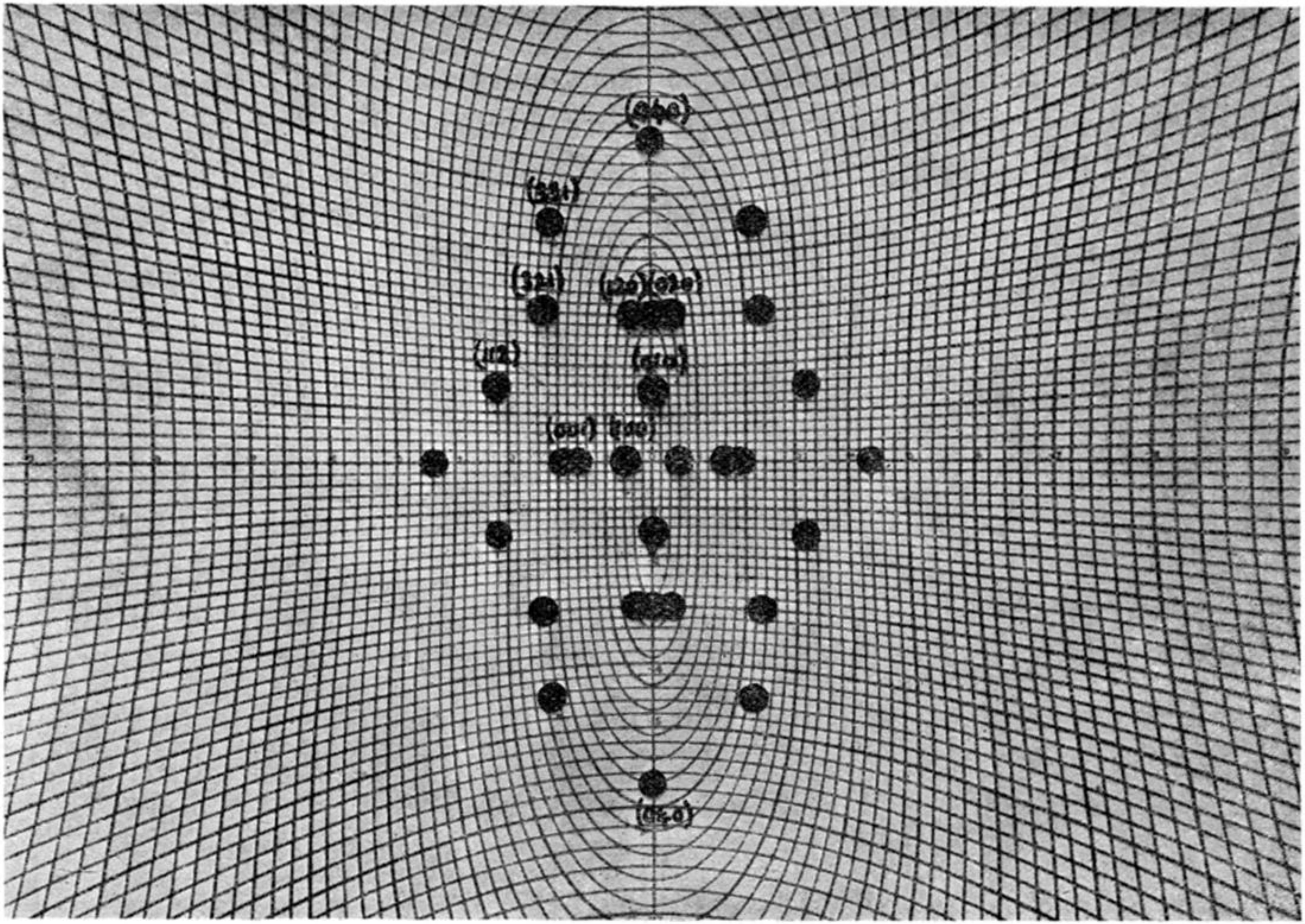


FIG. 1.—Hair. α-form.

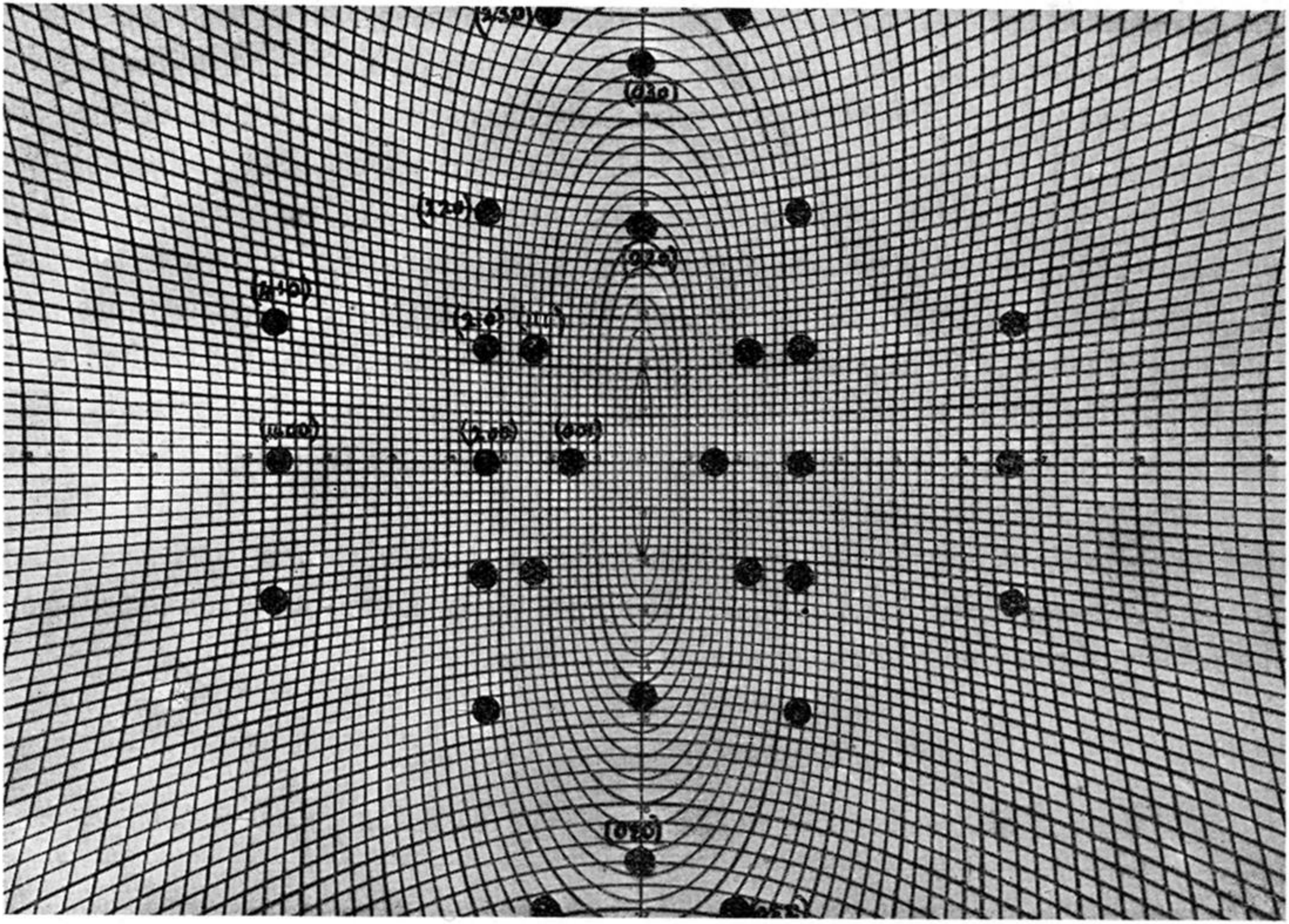
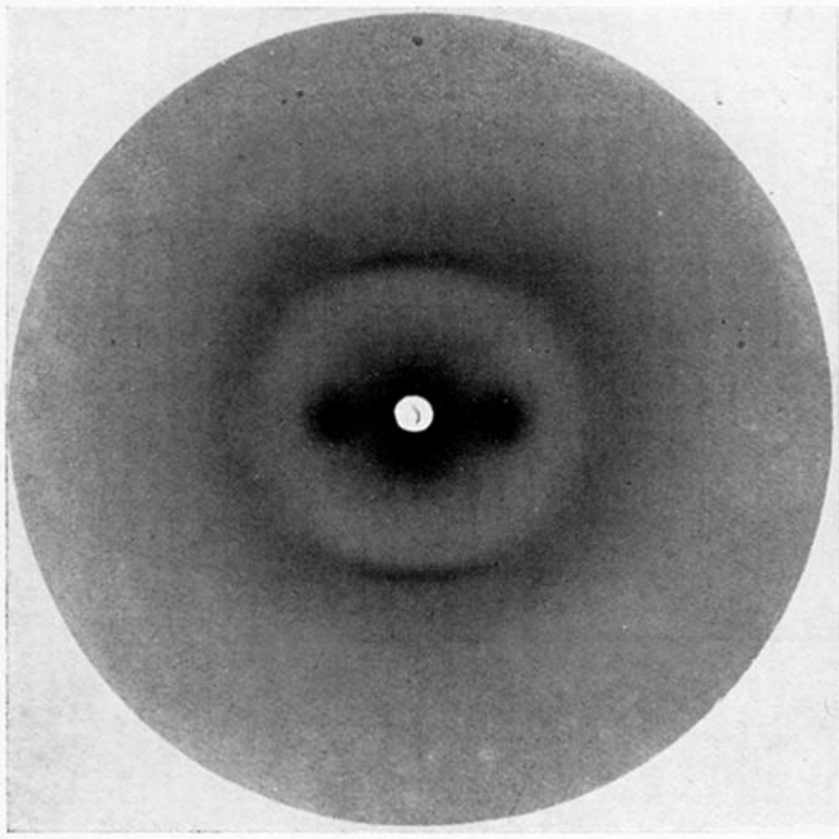


FIG. 4.—Hair, β-form.



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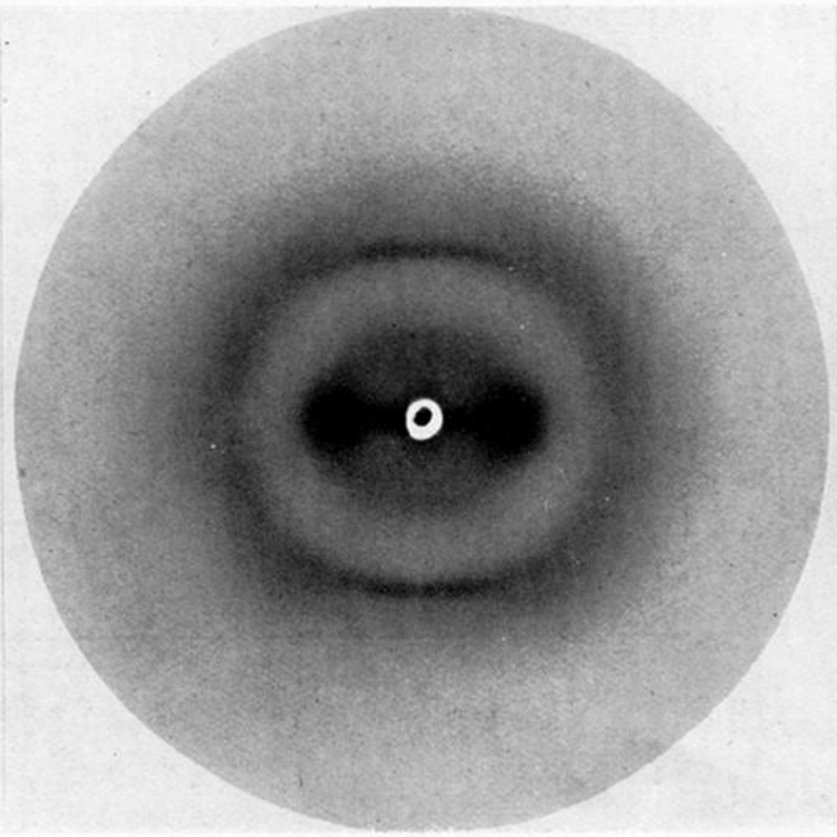

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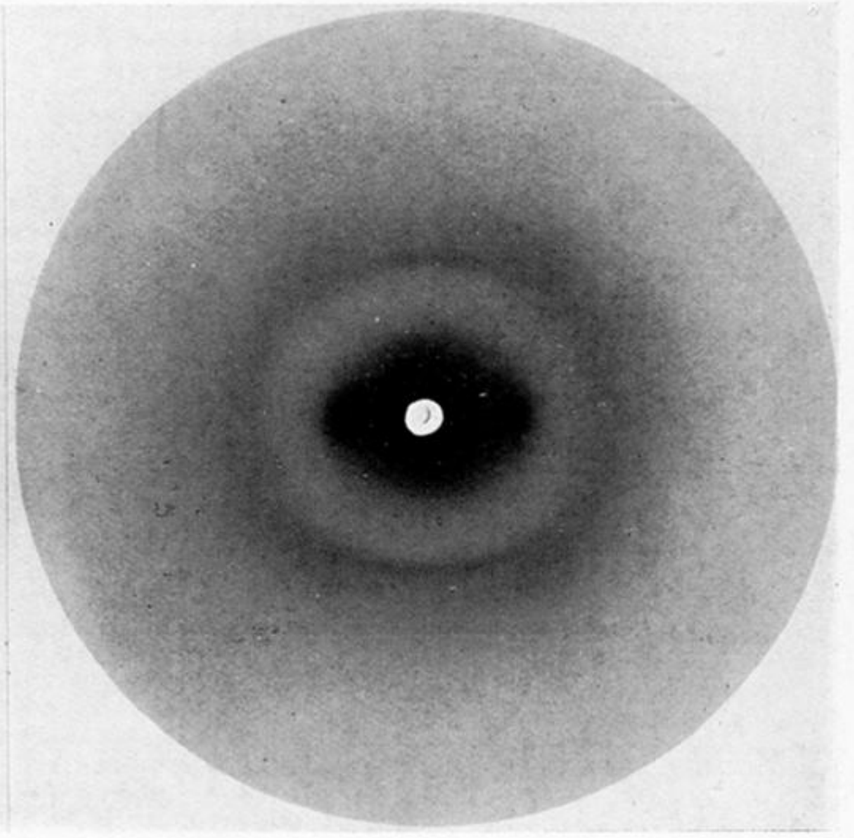

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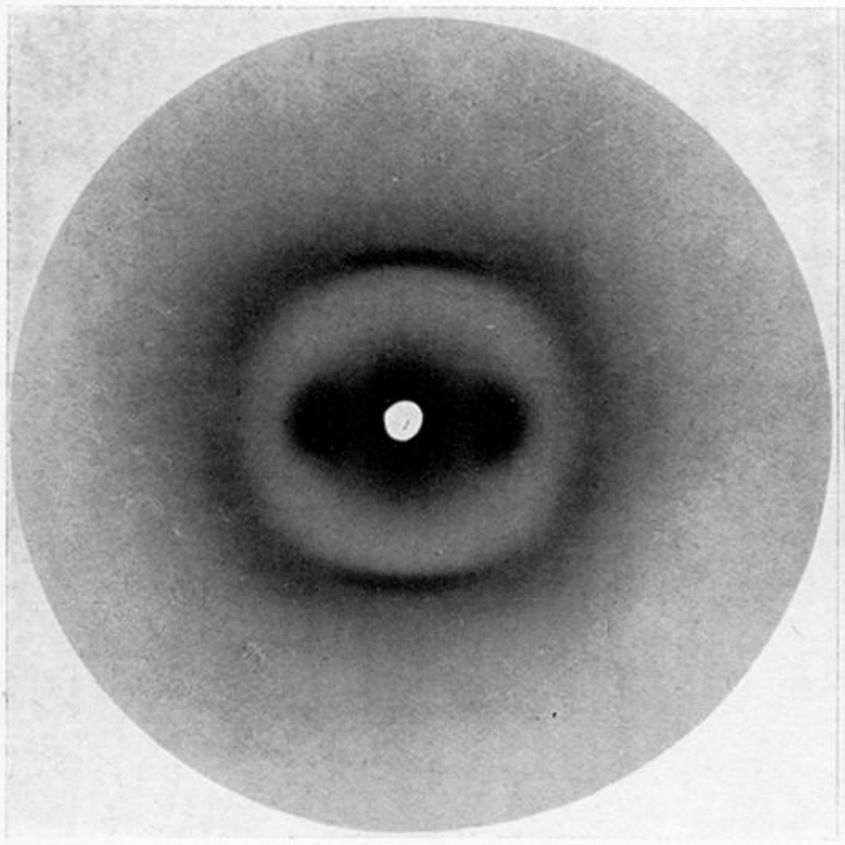

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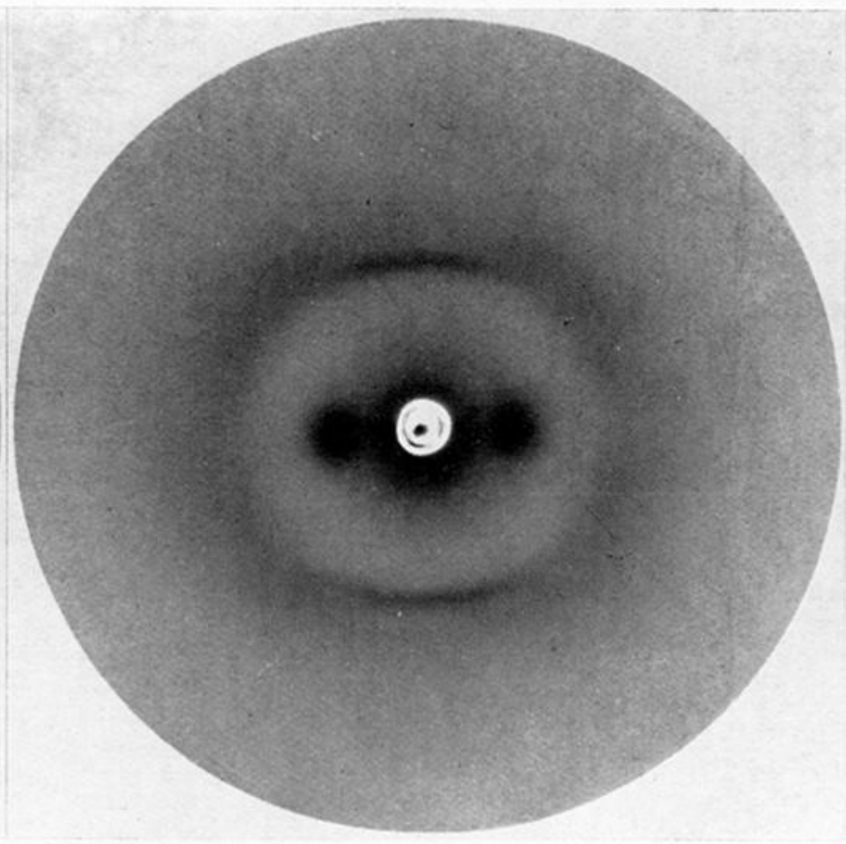

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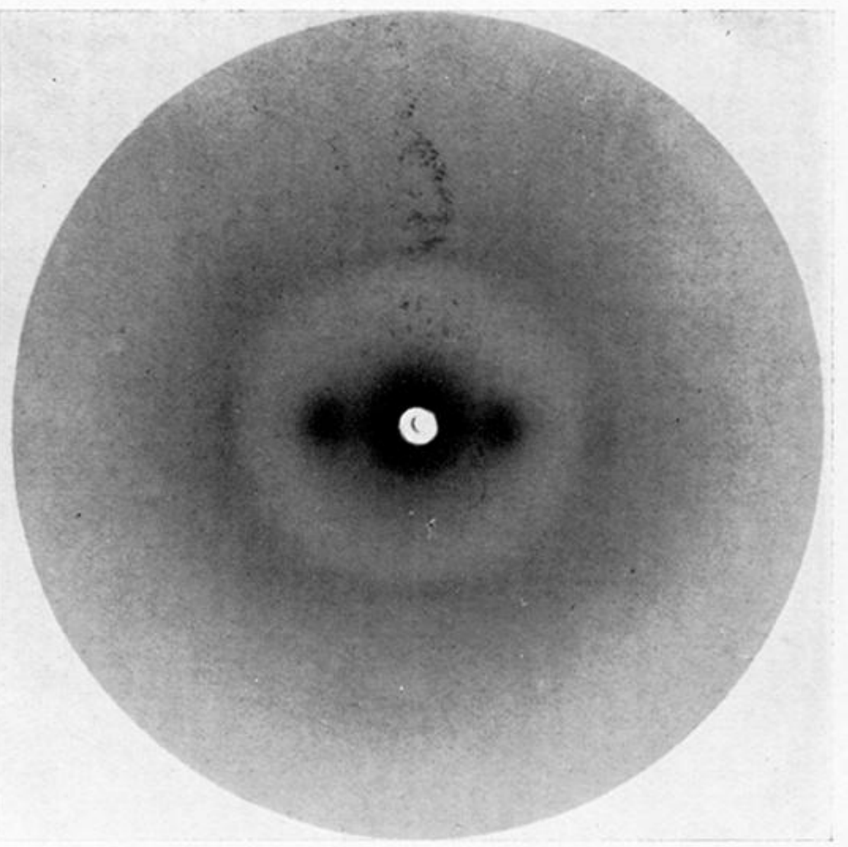

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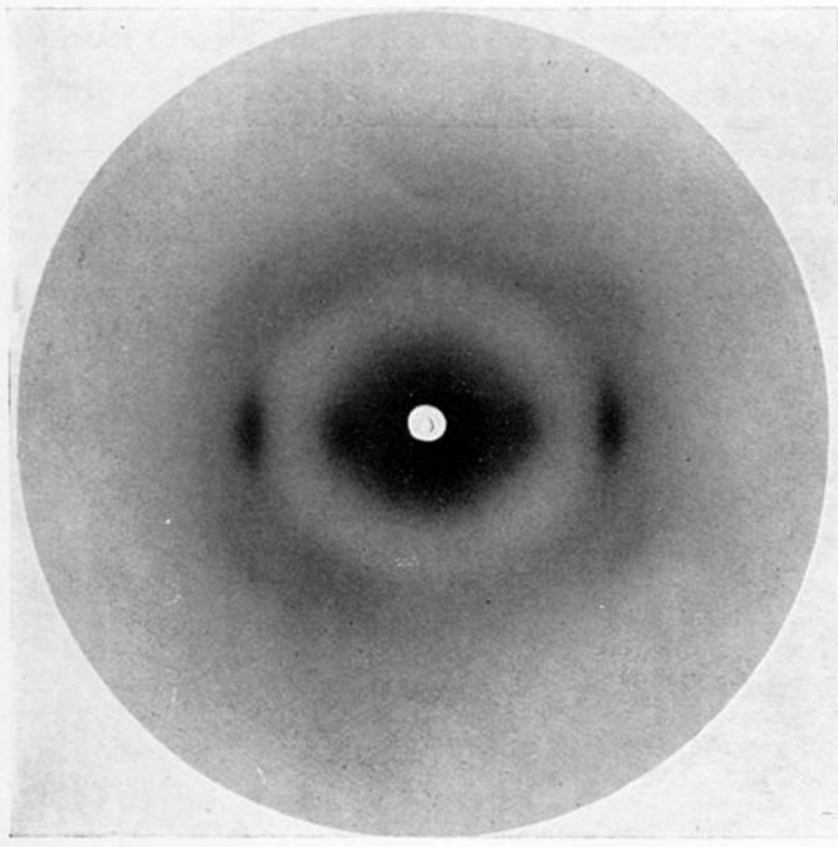

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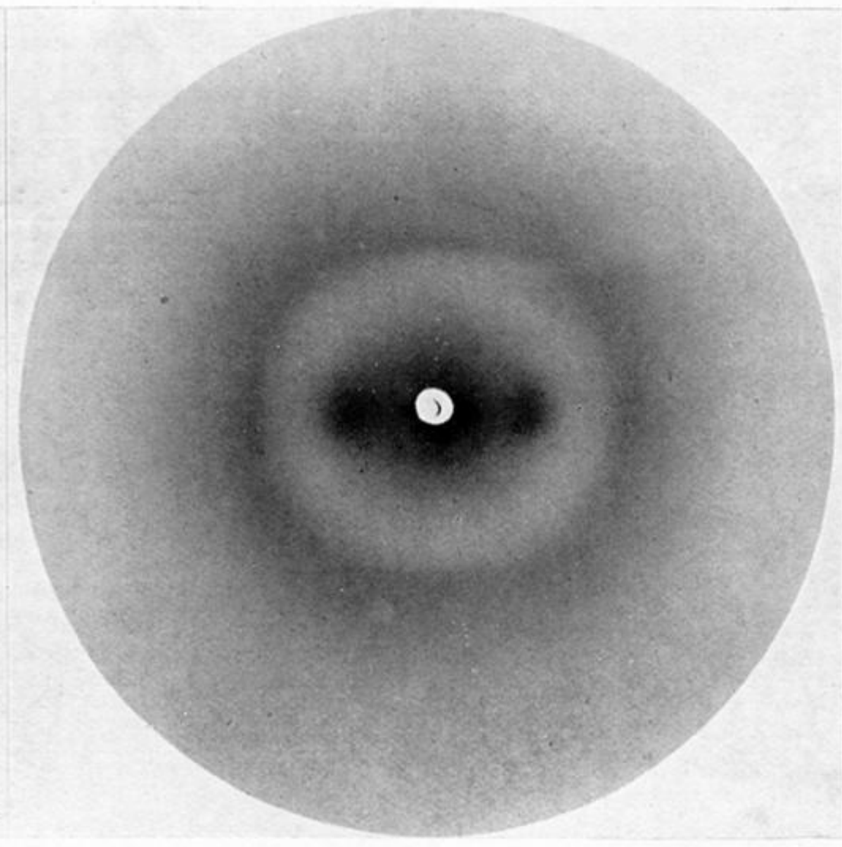

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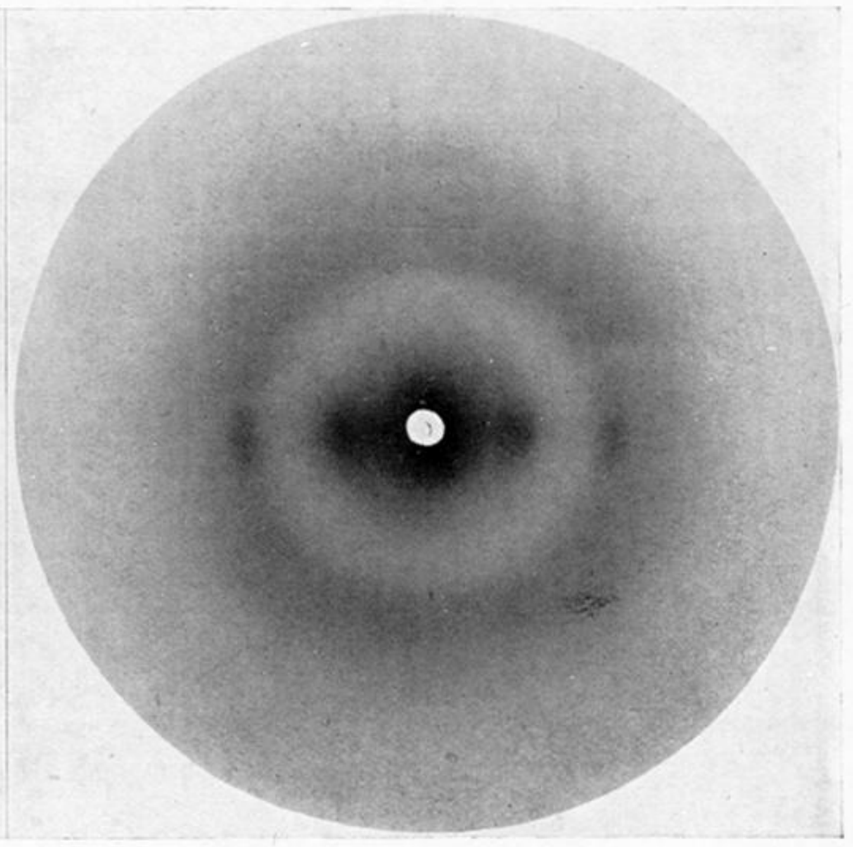

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Merino wool fibre
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