July 14, 1925. 1,546,349

A. W. HULL ET AL

X-RAY DIFFRACTION APPARATUS

Filed Oct. 10, 1921 2 Sheets-Sheet 1

Fig. 1.

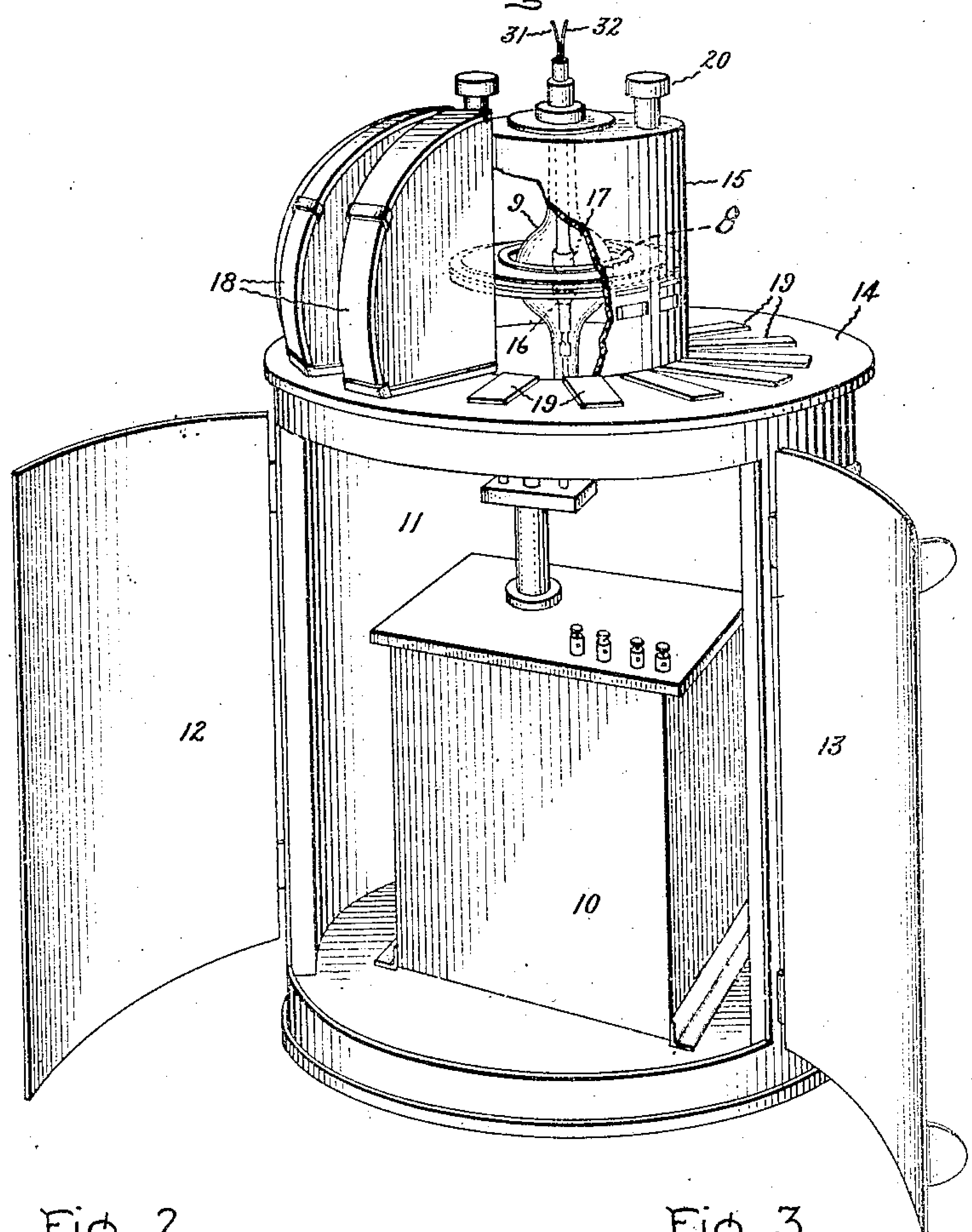

Fig. 2.

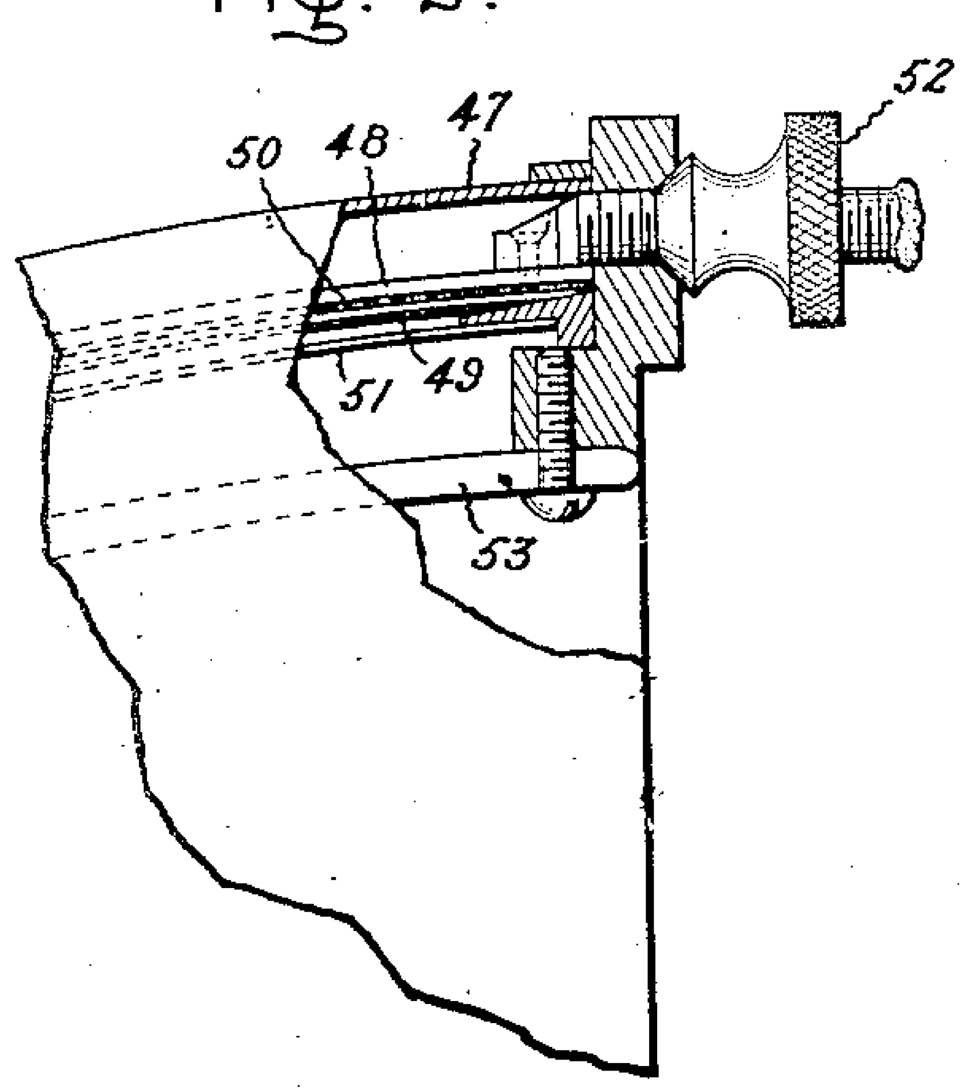

Fig. 3.

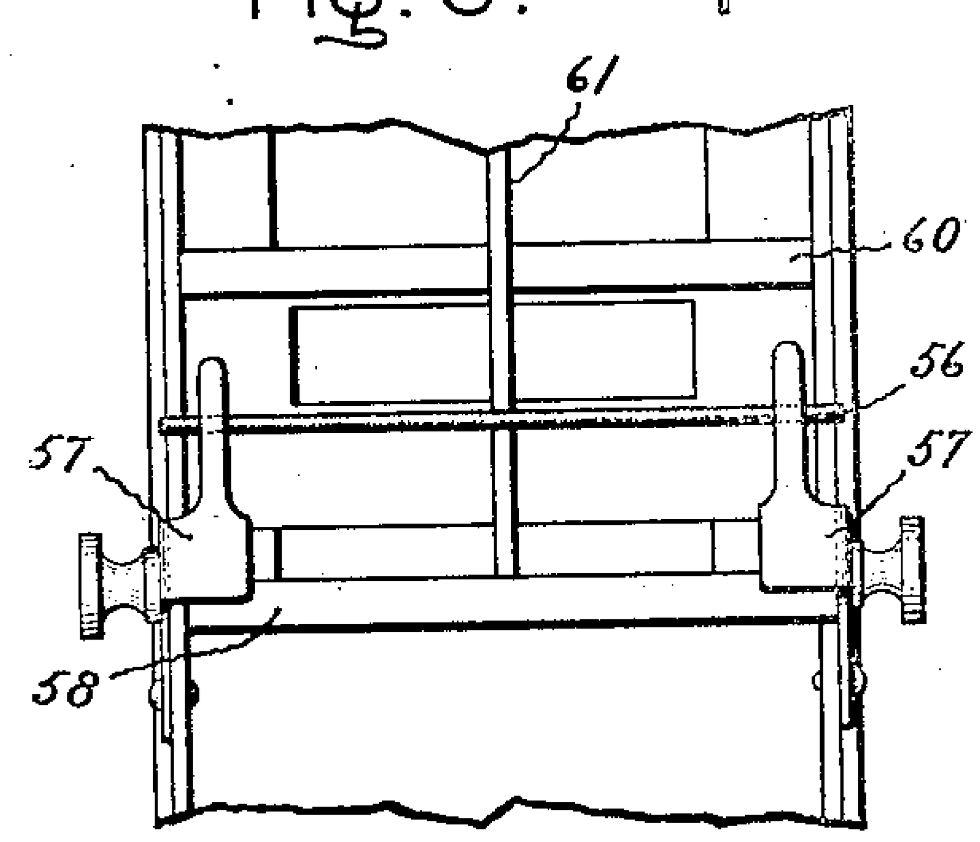

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Fig. 7.

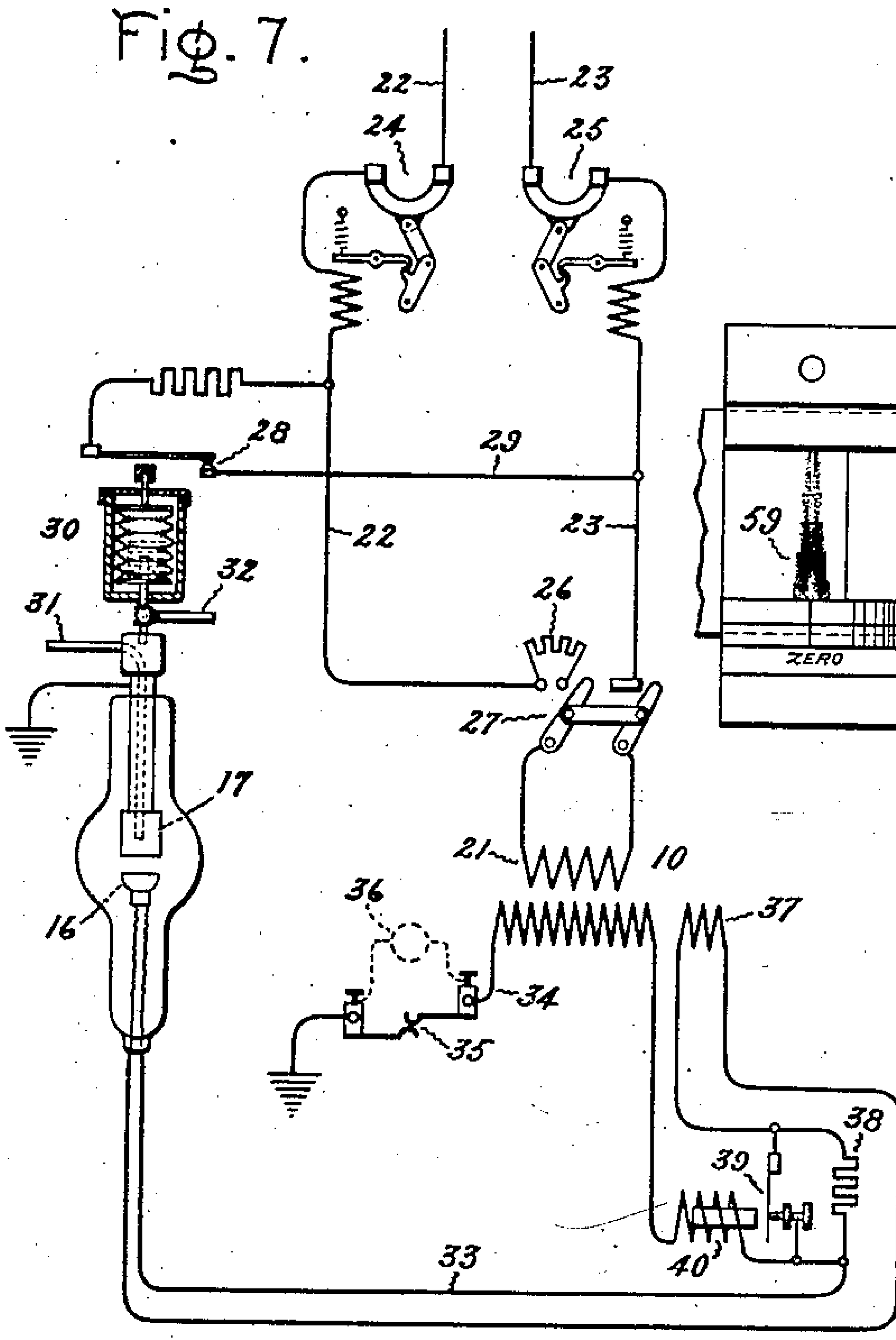


Fig. 8.

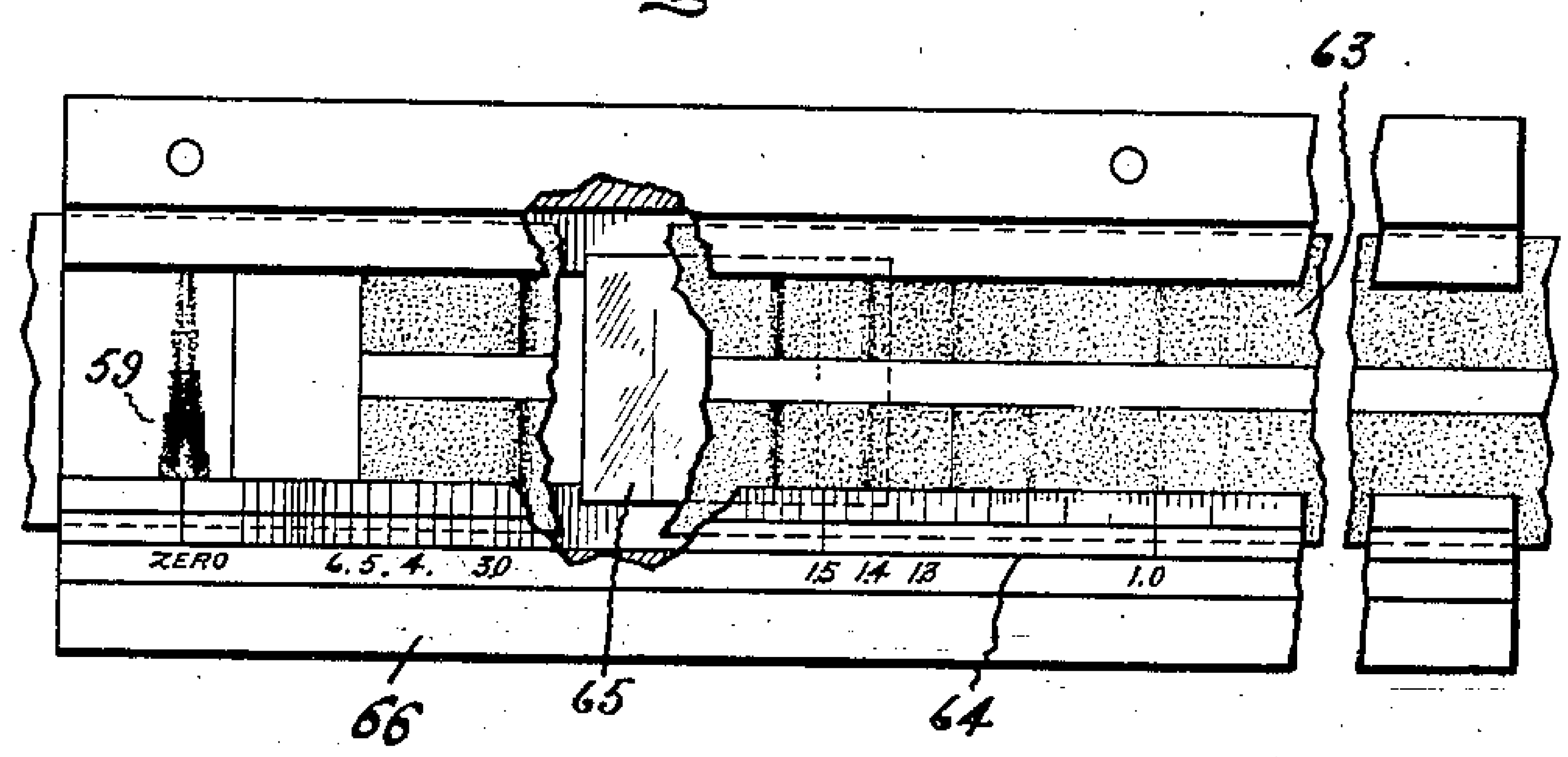


Fig. 5.

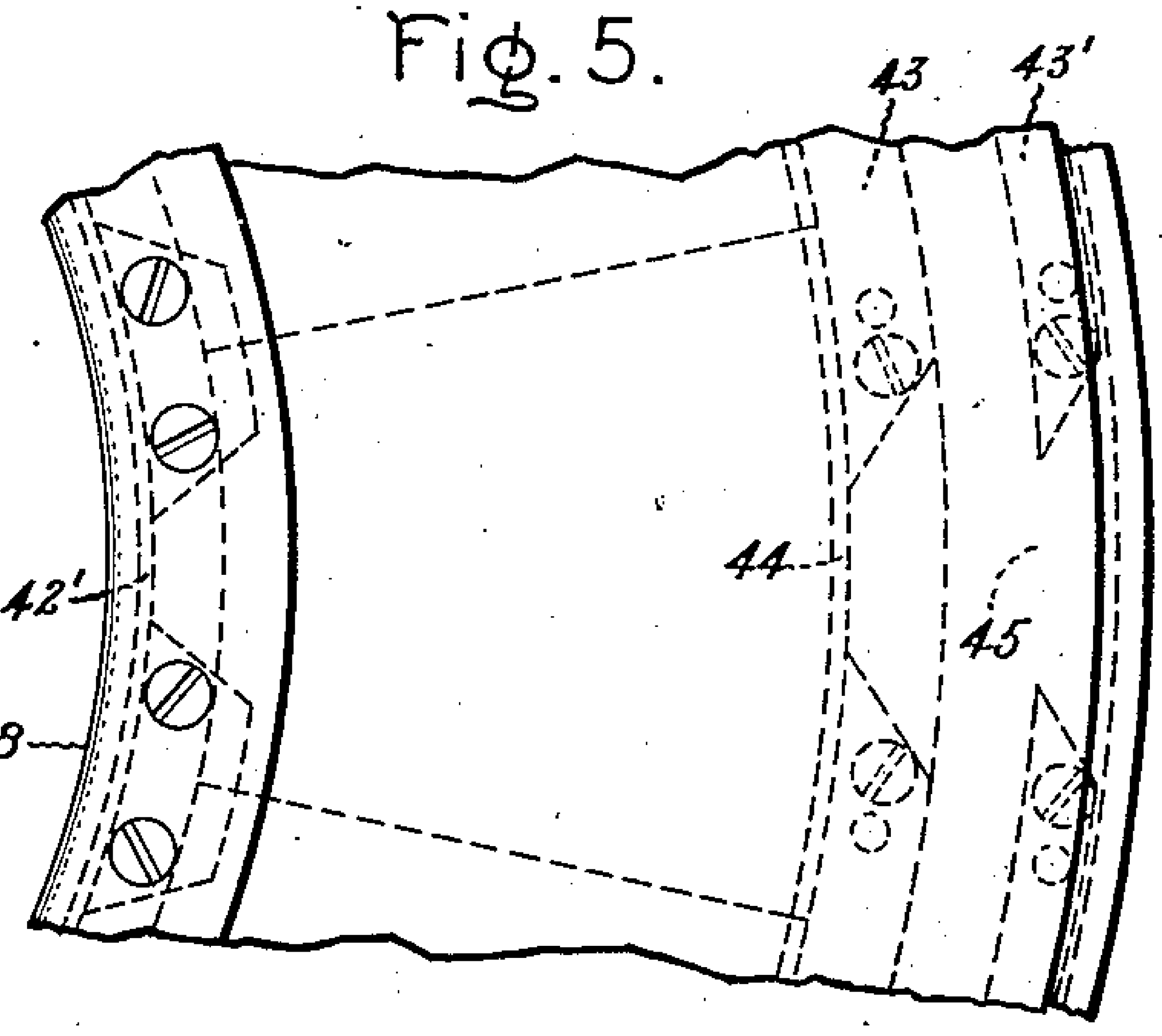


Fig. 4.

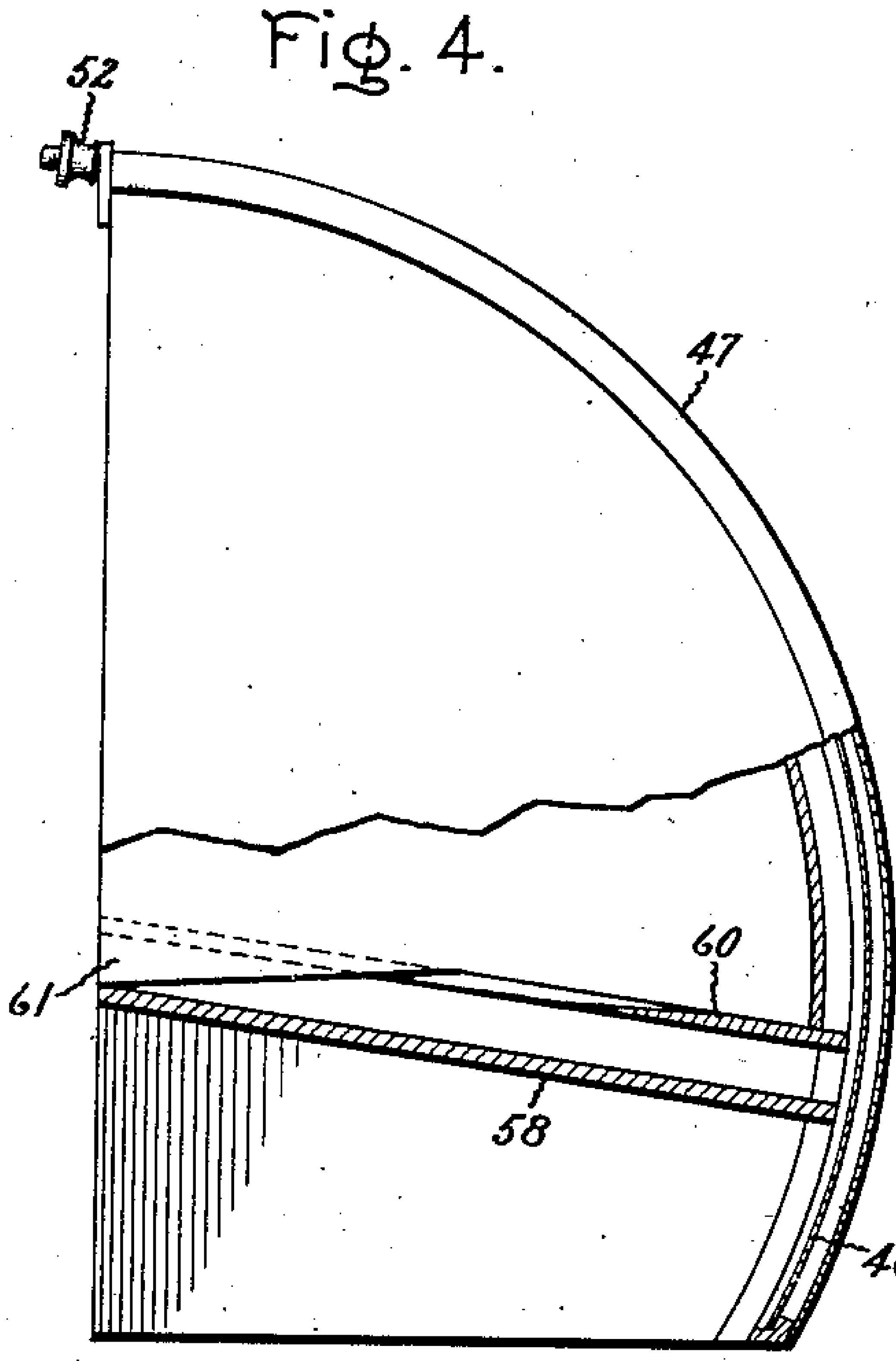
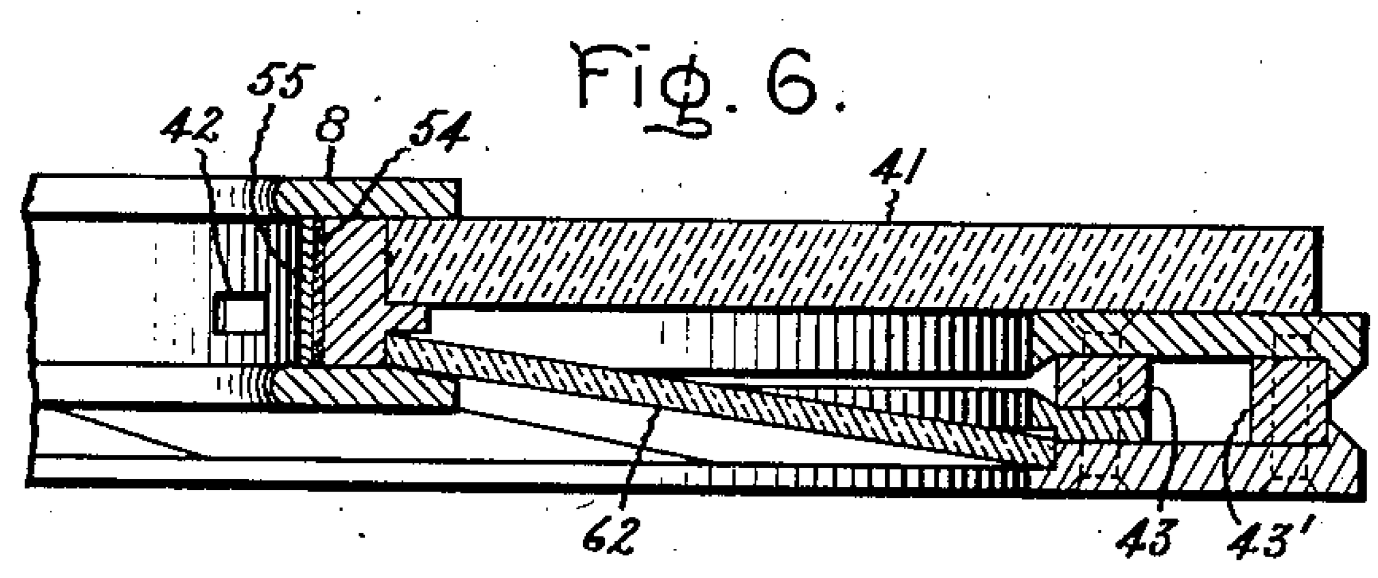


Fig. 6.



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UNITED STATES PATENT OFFICE.

ALBERT W. HULL AND WHEELER P. DAVEY, OF SCHENECTADY, NEW YORK, ASSIGNORS TO GENERAL ELECTRIC COMPANY, A CORPORATION OF NEW YORK.

X-RAY DIFFRACTION APPARATUS.

Application filed October 10, 1921. Serial No. 506,856.

To all whom it may concern:

Be it known that we, ALBERT W. HULL and WHEELER P. DAVEY, citizens of the United States, residing at Schenectady, in the county of Schenectady, State of New York, have invented certain new and useful Improvements in X-Ray Diffraction Apparatus, of which the following is a specification.

This invention comprises an improved apparatus for identifying crystalline materials by X-rays.

It has been found that, when X-rays are transmitted through a crystal or are reflected from the face of a crystal under suitable conditions, diffraction of the X-rays occurs, quite similarly to the diffraction of light rays by a diffraction grating. An X-ray diffraction pattern is obtained which is characteristic of the structure of the crystalline substance under examination.

Our invention comprises an improved apparatus particularly adapted to carry out the method of X-ray crystal analysis as described by one of us in the Physical Review, Vol. 10, page 661, 1917. In accordance with this method a substantially monochromatic beam of X-rays is transmitted thru a powdered mass of the crystals to be identified and the diffraction pattern thus obtained is recorded on a photographic surface. The pattern consists of a series of lines spaced apart, the spacing of the lines being determined by the spacing of the planes of atoms in the crystalline substance under examination. The number and spacing of the lines is as characteristic of the material of which the crystal is composed as are any other inherent properties such as density, solubility, melting point or ability to form chemical compounds.

In accordance with our present invention we have provided an apparatus which is particularly adapted for carrying out crystal analysis in a simple, expeditious manner without requiring specialized training on the part of the operator. Among the novel features of our improved device are the following:

The device provides means for producing a photographic record from which the distances between the crystal planes may be read off directly without calculation, thus providing a ready means for the identification of the material of which the crystal is composed.

Diffraction patterns of a number of crystalline substances may be recorded at the same time under substantially identical conditions, so that all variables are eliminated and the resulting patterns may be compared by the use of the same standard.

The apparatus is arranged to guard against accidental contact with electrical parts of high potential and the apparatus may be operated without supervision.

The apparatus is constructed to reduce corona and the consequent danger of accidental puncture of the X-ray tube.

These and other features of our invention will be set forth in the appended claims and explained with greater particularity in the following specification taken in connection with the accompanying drawings.

In the drawings Fig. 1 is a perspective of the apparatus as a whole; Figs. 2 to 6 inclusive are detail views of parts of the apparatus; Fig. 7 is a diagram of the electrical connections, and Fig. 8 illustrates a photographic record of an X-ray diffraction pattern and a scale for measuring the pattern.

As shown in Fig. 1, the apparatus comprises an X-ray tube 9 and a source of electric energy represented by a transformer 10, both contained in a housing 11 having doors 12, 13. The cathode end of the X-ray tube is connected to one terminal of the transformer, the tube projecting vertically thru the platform 14 into the turret 15, constituting an extension of the housing. Affixed within the turret 15 opposite the electrodes 16, 17 of the X-ray tube are a plurality of screens or diaphragms containing a slit system (see Figs. 5 and 6) whereby desired beams of X-rays are permitted to emerge from the turret as hereinafter more fully described. Grouped about the turret 15 are a plurality of cassettes 18, some of which are shown in position in Fig. 1. The cassettes in which the photographic records are made have a uniform size and shape and are adapted to be interchangeably positioned upon the guides 19 which are radially arranged about the turret on the platform 14, in order that a given crystal specimen will give an identical pattern whatever guide the cassette on which the specimen is mounted may be placed. A blast of air to cool the X-ray tube may be delivered by conduits not shown, the air leaving the turret thru the windows and exhaust tubes 20.

The preferred electrical connections for the X-ray tube are shown in Fig. 7. The electrical energy for operating the tube is derived from the transformer 10. The primary of this transformer receives power from conductors 22, 23 containing circuit breakers 24, 25 and a series resistance 26. When the double pole switch 27 is closed, the resistance 26 is first included in series with the primary and upon the further movement of the switch 27 is short circuited. A contactor 28 is included in a circuit 29 which is in shunt to the primary 21 of the transformer. When the contactor 28 is closed the X-ray tube is deenergized. This contactor is adapted to be held open during the operation of the X-ray tube by a pressure responsive device 30 operated by the pressure of the cooling water for anode 17 in the circulating system represented by the conduits 31, 32. If for any reason the supply of cooling water is interrupted, then the operation of the device 30 automatically short circuits the current supply for the X-ray tube.

The anode 17 is grounded, as indicated, the cathode 16, which comprises a heated filament (not shown) and a surrounding focusing device, is connected to one terminal of the secondary of the transformer 10 by a conductor 33, the opposite terminal of the transformer secondary being grounded thru a conductor 34. If desired the conductor 34 may contain contacts 35 separated by a thin dielectric, such as a sheet of paper. In shunt to these contacts is connected a milliammeter 36. Should the milliammeter be removed while the device is in operation the dielectric will be punctured.

The cathode 16 is supplied with heating current by a transformer secondary winding 37 containing a resistance 38. Preferably a vibrating regulator 39 is provided to periodically short circuit the resistance 38 in response to current in a winding 40 so as to regulate the electron emission of the cathode in such a way that the current throughout the tube remains substantially constant. This regulator is no part of our present invention.

The anode 17 preferably consists of molybdenum and the face of the anode receiving the discharge from the cathode is symmetrical with respect to the major axis of the tube so that the X-rays are uniformly distributed with respect to the vertical axis.

The screen system for producing the desired beams of X-rays is indicated in Fig. 1, but is more clearly shown in Figs. 5 and 6. Adjacent the X-ray tube is provided an annular diaphragm 8 consisting of suitable metal which is supported by a plate 41 consisting of glass or other suitable dielectric material. The outer periphery of the plate 41 is supported by diaphragms 43, 43′ which in turn are supported by the turret 15. The diaphragm 8 is insulated from the rest of the apparatus in order to prevent damage to the X-ray tube, by puncture thru the glass. This diaphragm 8 contains a plurality of horizontal slits, one of which is indicated at 42 in Fig. 6 and another at 42′ in Fig. 5, which is a plan view of a portion of this slit system. Surrounding the diaphragm 8 are diaphragms 43, 43′, as best shown in Fig. 5. Opposite the slits in the diaphragm 8 and in line therewith, as shown in Fig. 5, are slits in the external diaphragms 43, 43′, as shown at 44, 45, so that the X-rays emerging from the X-ray tube, making a small angle of 5 to 10° with the face of the anode 17, emerge through the three slits in sequence and then through one of the windows of the turret. The slit 44 is somewhat wider than the slit 42 as the X-ray beam is divergent. The slit 45 is made considerably wider than the slit 44. Its function is only to cut off rays which are diffracted at the edges of the slit 44.

The narrow horizontal beams of X-rays emerging from the windows in the turret 15 through this slit system are utilized to form X-ray diffraction patterns upon photographic films mounted in vertical arcs in the cassettes 18. As the X-ray beams emerge at a uniform angle with respect to the vertical axis of the apparatus and the slits are of uniform size and spacing, the cassettes 18, which are radially arranged about the X-ray tube, may be made interchangeable. The photographic records produced in any of the cassettes may be measured by the same standard.

The cassettes, as best shown in Figs. 2, 3 and 4, comprise boxes made of brass, or other suitable material having a removable arc-shaped cover 47. Adjacent the cover is a flexible brass plate 48 (see Fig. 2) under which a photographic film 49 is held in position between a layer of felt 50 and a strip of paper 51 by a thumb screw 52. Between the photographic film and the source of X-rays is a filter 53 consisting of zirconium oxide, or other material selective to the X-rays of desired wave length so as to obtain a beam of substantially monochromatic X-rays. A filter 54 is preferably also provided adjacent the slits in the diaphragm 8. As shown in Fig. 6 this filter 54 is held in position by a thin metal strip 55.

The material to be tested preferably is

contained in a powdered state, within a small glass tube 56 held in position by clips 57 on the vertical part of the cassette opposite the slit system so as to be traversed by the respective horizontal beams of X-rays. The cassettes preferably are provided, with a transverse partition 58 (Fig. 4) separating the same into two compartments. The end of the film exposed to the direct or undiffracted X-rays passes behind a series of overlapping plates (not shown). The record on the film in the lower compartment serves in the well known way as a measure of exposure, because it consists of a series of graduated shadows which may be compared with various lines comprising the diffracted pattern. However, this comparison standard is not essential as the same purpose may be served by the portion of the undeviated beam of X-rays at the zero position on the film as indicated at 59, Fig. 8. This zero of reference on the film is also made by the X-ray beam passing through a series of overlapping plates to provide some portion of the reference mark with a radiographic exposure of such depth as to permit of exact measurements. A metal tongue 60, Fig. 4, screens the edges of the entering beam at the zero position from the upper portion of the photographic film, in order to prevent fogging of the film due to secondary X-rays.

A longitudinal partition 61 may be provided to enable two exposures to be made on a single film as indicated in Fig. 8. The patterns indicated on the film in Fig. 8 are identical as may be the case when it is desired to check the composition of two substances which should be identical. The glass plate 62, Fig. 6, prevents secondary X-rays from the turret from entering through the slit system and striking the specimen and film.

When the substances to be examined are mounted on the cassettes and the cassettes are positioned on the platform 14, as indicated in Fig. 1, the X-rays tube is energized to generate X-rays characteristic of the target and the exposure is continued from 5 to 70 hours, the length of time depending on conditions.

The X-rays are diffracted by the crystalline powder over a wide angle extending as far as 180°. The diffracted rays produce upon the photographic film a spectrum-like pattern varying with the crystalline constitution of the substance under examination, as described in the above noted Physical Review article. As shown in Figs. 1 and 4, the strip of film is supported in an arc of a circle the centre of which lies in the crystalline material to be tested and which intercepts rays over an angle of about 90°. A pattern obtained with sodium chloride is indicated in part at 63, Fig. 8. It may be measured for interpretation by a scale 64 marked in such a manner that when the reference mark 59 is set opposite the "zero line" of the scale, the lines in the pattern may be read off directly from the scale in terms of the interplanar spacings in Angstrom units in the crystal under examination.

As explained by Bragg and Bragg in their book on "X-Rays and Crystal Structure," 1916, Chapter II, the formula of diffraction is as follows:

$n\lambda = 2\ d \text{ sine } \theta.$

n=the order of the diffraction pattern.

λ=the X-ray wave length.

d=the interplanar distance.

θ=the angle made by the diffracted beam of X-rays with the plane of atoms in the crystal. It is half the angle θ between the incident and diffracted beams.

Hence

$n\lambda = 2\ d \text{ sine } {}^{\theta}/_{2}$

$= 2\ d \text{ sine } \tfrac{1}{2} r.$

ϕ=the angle between the incident and the diffracted beams of X-rays, which may be measured as the quotient of the length of the arc divided by the radius. This gives the angle in radians.

L=the distance along the photographic film from the record of the undeviated beam, that is, the length of the arc referred to above to the record of the diffracted beam.

r=the radius of the arc in the cassette along which the photographic film is bent.

The scale 64 was derived as follows: From the value of λ and the radius "r" of the cassettes, the distance "L" along the photographic film from the undeviated beam of the diffracted beam was calculated for different interplanar spacings "d". These distances along the film calculated in this way were marked as a scale on a holder 66 for the film on which the position of the undeviated beam marked the zero or reference position.

A glass slide 65 having a marker consisting of a vertical scratch (preferably broken) as indicated, may be used to conveniently find the position of the lines on the film, the marking on the slide being placed on the center of a line when viewed by transmitted light and its position on the scale then being noted. These interplanar distances may be compared with distances already measured on known materials and the unknown may be thus identified.

What we claim as new and desire to secure by Letters Patent of the United States, is:

1. An X-ray diffraction apparatus comprising the combination of means for producing a beam of substantially monochromatic X-rays, means for supporting material to be examined in the path of said beam and means for supporting a photographic film in an arc of a circle exposed

to the rays diffracted by transmission of said beam through said substance.

2. An X-ray diffraction apparatus comprising the combination of means for producing a horizontally extended beam of substantially monochromatic X-rays, a movable cassette providing arc-shaped means for recording a diffraction pattern produced by the transmission of said beam through a cyrstalline substance, and means for predetermining the operative position of said cassette in order that any given substance will produce the same pattern for different exposures.

3. An X-ray diffraction apparatus comprising the combination of means for producing X-rays, a screen opaque to X-rays having a horizontal slit for transmitting a beam of X-rays, means for supporting a substance to be tested in the path of said beam and means for supporting a photographically sensitive medium in an arc of a circle which intercepts the diffracted rays over a wide angle, whereby a characteristic X-ray diffraction pattern made by the diffraction of X-rays by said substance may be recorded.

4. An X-ray diffraction apparatus comprising the combination of means for producing a plurality of narrow beams of X-rays, radial with respect to a common axis, emerging at substantially a uniform angle with respect to said axis, and a plurality of cassettes supported respectively opposite said slits, each of said cassettes providing a holder for supporting a photographically sensitive medium and means for supporting material to be tested.

5. An X-ray diffraction apparatus comprising the combination of an X-ray tube having a symmetrical structure about a longitudinal axis passing thru the electrodes, a housing impervious to X-rays having a plurality of windows symmetrically spaced about said tube, a diaphragm between said tube and said housing having slits transmitting beams of X-rays thru said windows, a platform surrounding said windows having a plurality of guides located adjacent to said respective windows, and a plurality of cassettes of uniform size and structure adapted to be interchangeably positioned upon the guides on said platform opposite said windows.

6. An X-ray diffraction device comprising the combination of a container substantially impervious to X-rays, a transformer therein, an X-ray tube mounted in a vertical position in said container, electrical connections between said tube and said transformer, a plurality of slits in a plane nearly coincident with the face of the anode of said tube, and a plurality of cassettes adapted to be positioned vertically opposite said respective slits.

7. A crystal analyzer comprising the combination of a container, a transformer therein, an X-ray tube having the cathode terminal electrically connected to said transformer, the anode terminal of the tube and the opposite terminal of the transformer being grounded, a grounded housing for said X-ray tube which is substantially opaque to X-rays and project above said container, a diaphragm in said housing having a plurality of slit systems radially disposed with respect to said tube and a plurality of cassettes adapted to be positioned upon the transformer housing opposite said slit systems and about said X-ray tube, each of said cassettes being adapted to support in a vertical plane a photographic film in an arc-shaped position so as to intercept a diffracted X-ray beam.

8. An X-ray diffraction apparatus comprising an X-ray tube, means for supporting said tube in a fixed position, means for limiting the X-ray radiation from said tube to a narrow beam, means for supporting a material to be examined in a fixed position in the path of said beam, means for filtering said rays to monochromatic rays, means for recording the resulting diffraction pattern of X-rays bent on an arc, and a scale having markings linearly displaced from the position of the record of the undeviated beam to correspond with the different values of L calculated from the formula $n\lambda=2d \text{ sine } \frac{L}{2r}$, λ being the wave length of said monochromatic rays, d the distance between planes of atoms in a crystal, and r the radius of the arc on which the recording means is positioned.

9. A scale for the interpretation of a record of X-ray diffraction patterns made by a beam of substantially monochromatic X-rays passing through a crystalline material and impinging on a photographic recording device supported in an arc of a circle in the path of a diffracted portion of said beam which consists in a holder for said record having markings representing different values of L calculated from the formula $n\lambda=2d \text{ sine } \frac{L}{2r}$ for different values of d (the interplaner distance) n being the order of the diffraction pattern, λ being the predominant X-ray wave length, r the radius of curvature of the photographic device, and L being the distance on the photographic record from the zero point determined by the undeviated beam and the point where a deviated beam would fall for a given value of d.

10. A cassette for an X-ray diffraction apparatus comprising a removable arc-shaped cover, means for supporting a photographic film adjacent said cover, means for supporting material to be sub-

jected to X-rays at the center of curvature of said film, and a partition in said cassette so positioned that a part of said film is screened from undiffracted secondary X-rays while receiving diffracted X-rays, said partition also being so positioned with respect to the incident beam of the X-rays as to permit a reference marking of said beam upon said film.

In witness whereof we have hereunto set our hands this 8th day of October 1921.

ALBERT W. HULL.
WHEELER P. DAVEY.