A method to determine the indicatrix of small crystals.

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[Communicated by Dr. F. A. Bannister; read January 26, 1950.]

Introduction.

IN the course of the investigation of the crystal structure of sodium-thyroxine-*dl* it appeared to be necessary, in order to find the approximate orientation of the molecule, to determine the orientation of the indicatrix and the values of the principal refractive indices.

The crystals are flat and very thin (about 0·03 mm. thickness), and when put on a glass slide they all lie on their (100) face. This suggested the use of the universal stage, but the high birefringence of the crystals prevented it from giving good results. Moreover, as the crystals belong to the triclinic system and have no regular contour, it would have been difficult to refer the indicatrix to the unit cell. The interference figures seen when the crystals lie on a glass slide were mis-oriented, though sufficient to determine the sign of the indicatrix, and no clear interference figures could be seen when the crystals were far from horizontal.

To overcome these difficulties the method which follows was developed, and proved to be very useful for all uniaxial crystals and highly birefringent biaxial crystals, whatever their habit.

The one-circle stage goniometer.

The crystal is mounted on a glass fibre (no particular orientation is necessary) at the end of the one-circle stage goniometer described by Bernal and Carlisle[1] (fig. 1). It is a very simple instrument, fits on any microscope stage, and enables one to rotate the crystal about a horizontal axis. Furthermore, a thin glass slide may be adjusted to the goniometer, underneath the crystal, and a drop of a liquid that does not attack the crystal and has a suitable refractive index may be put on it, so as to have the small crystal completely immersed. The mounting of the crystal has to be done carefully, so as to enable its free rotation in the liquid, not far from the glass slide but without touching it.

[1] J. D. Bernal and C. H. Carlisle, Journ. Sci. Instruments, London, 1947, vol. 24, p. 107.

The end of the crystal holder *A* of the goniometer may be unscrewed and adapted to the holder of an X-ray diffraction camera, without changing the mounting of the crystal. As will be seen later, this makes it very easy to refer the axes of the indicatrix to the unit cell of the crystal, and also enables one to use this method as a help for setting crystals for X-ray diffraction photographs.

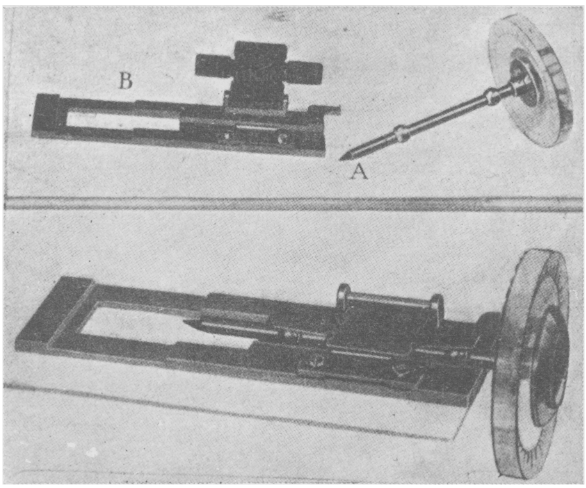

FIG. 1. The one-circle stage goniometer. (Reproduced from the Journal of Scientific Instruments.)

General considerations.

When a crystal is in a given position (on a polarizing microscope, crossed nicols, parallel light), the two observed extinction directions are the axes of the ellipse determined by the intersection of the indicatrix with the plane of the microscope stage, and the magnitudes of these axes are given by the corresponding two refractive indices. Errors arise if the incidence is not normal, due to the deviation of the wave-front, and especially if the crystal has a complex habit. No such errors appear when the crystal is immersed in a liquid whose refractive index is equal to that of the crystal in the observed vibration direction.

Now, for each position (θ) of the goniometer, there are two extinction directions (ϕ_1 and ϕ_2 perpendicular to each other), given by the corresponding readings of the microscope stage, or polarizer-analyser system in some models. These extinction directions can be represented on a stereographic projection at suitable intervals of θ (fig. 2). The primitive is the great circle $\theta = 0°$, and on it the two ϕ readings for the initial position of the crystal are marked, taking as origin the intersection of the primitive with the rotation axis of the crystal. The whole is adjusted so that when $\phi = 0°$ the light transmitted by the polarizer vibrates parallel to the rotation axis of the crystal.

If the goniometer is now turned by a given angle, for instance, 10°, the great circle $\theta = 10°$ will come into the horizontal, and there will be the two corresponding ϕ readings.

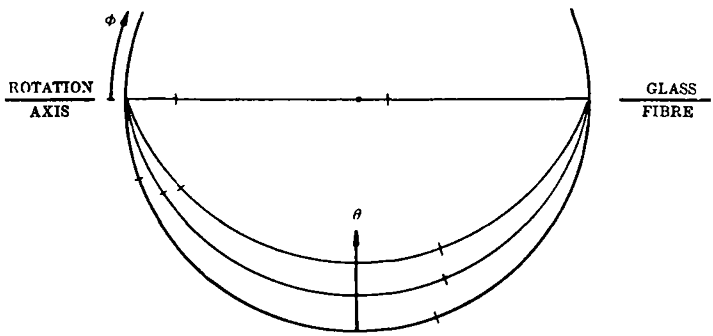

FIG. 2. Extinction directions in stereographic projection. The great circles $\theta = 0°$, 10°, 20°, and 90° are shown, with the two extinction directions on each.

In the stereographic projection, each value of θ is represented by a great circle through the goniometer axis; and on those great circles, with the help of a stereographic net, the ϕ readings are inserted. The angle θ is measured in the sense opposite to that of the rotation of the crystal, the sense of ϕ depending on the geometrical arrangements. During a complete rotation of the indicatrix about its fixed (but arbitrary) axis, these two sets of points determine, on the indicatrix and on the stereographic projection, a centro-symmetrical set of curves.

It is clear that every vector of the indicatrix will eventually come into the horizontal plane during this rotation; hence, it is possible to bring into the horizontal plane each one of the three axes in turn.

As each axis of an ellipsoid is a two-fold axis, every central section that contains one of the three axes has this axis as an axis of symmetry. This is particularly easy to see for the X and Z axes. As γ along the Z axis is the longest vector of the ellipsoid, it must also be the longest vector of any ellipse that contains it, and hence, is the longer axis of that ellipse. The same argument applies to the X axis, α being the smallest refractive index. It follows that, as soon as one of the three axes of the indicatrix comes into the horizontal plane, it becomes one of the two axes of the observed ellipse, and therefore the points representing the three axes of the indicatrix lie on the curves of the extinction directions. In other words, that set of curves contains the points representing the axes X, Y, Z of the indicatrix.

The axes will be located if the position of one of them is determined. That may be done by finding the particular vibration direction in the crystal for which the refractive index is a maximum or a minimum.

Experimental procedure.

There are two independent steps: (*a*) the determination of the stereogram of the extinction directions, and (*b*) the determination of the direction of maximum (or minimum) refractive index.

(*a*) From the above considerations and the study of fig. 2, it is quite clear how the stereogram may be drawn, taking θ at suitable intervals, for instance, 10°. During this operation, which requires only a very short time, there is no liquid on the goniometer glass slide.

(*b*) To find the direction of maximum (or minimum) refractive index, a drop of a suitable liquid of known refractive index (near to the one expected to be found for the crystal) is put on the glass slide of the goniometer, so as to have the small crystal completely immersed in it. By successive rotations of the goniometer, and by putting the crystal each time in extinction position, the vibration direction (or directions) for which the crystal has a refractive index equal to that of the liquid is determined with the method of the Becke line. It is easy to discover now (also with the Becke-line effect), on which side of the determined vibration direction the refractive index increases (or decreases), or in which region between two determined directions of equal refractive index the maximum (or minimum) has to be found, and a liquid of higher (or lower) refractive index is tried, after having carefully removed the first one with a filter paper, without touching the crystal. This is repeated—in general two or three attempts will be sufficient—till the maximum (or minimum) is found with the help of standard liquids or mixtures of them if necessary. This gives us, at the same time, the direction of the axis and the value of the corresponding refractive index.

Biaxial crystals.

Let us discuss the case of a positive crystal, in which the direction of the Z axis (γ) is determined first. (On a negative crystal it is better in general to start with the X axis (α), the minimum refractive index direction.) The direction of the Z axis (θ and ϕ) is put into the stereographic projection and the great circle perpendicular to it is drawn (fig. 3). This circle will intersect the extinction direction curves at points (90° away from each other) that are the X and Y axes of the

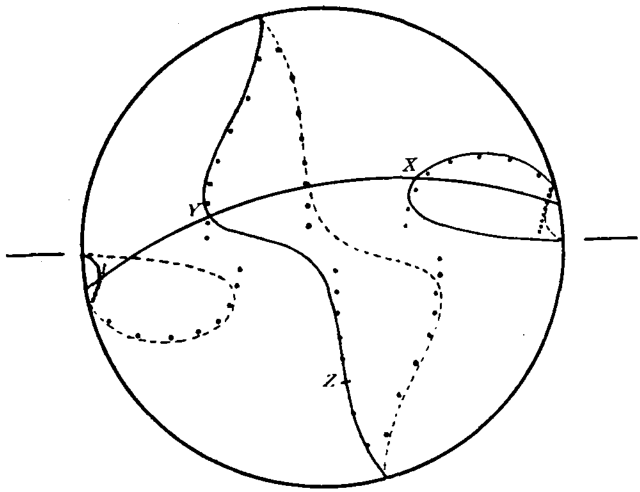

Fig. 3. Extinction directions in a biaxial crystal. Experimental points (crystal rotating in air), and theoretical curves. Also the great circle perpendicular to Z is shown.

indicatrix. Hence, it will be sufficient to determine the extinction directions in the region perpendicular to the Z axis. In some favourable cases, only a small number of points is required (it depends on the particular rotation axis of the crystal) but, even if the whole indicatrix is explored (θ from 0° to 180°), it takes only a very short time.

The X and Y axes are thus determined; and each one of them is brought into the horizontal plane, to measure α and β respectively. The direction of the X axis will be checked when measuring α, as it must be the minimum refractive index direction.

Now, X-ray diffraction photographs will enable the axes of the indicatrix to be referred to the unit cell of the crystal. For this purpose, the end of the crystal holder of the goniometer is unscrewed, and adapted to the holder of a diffraction camera, without changing the relative positions of the crystal, the glass fibre, and the end of the holder.

It should be noted that the experimental points in the stereogram of fig. 3 are affected by errors due to the deviation of the wave-front when incidence is not normal. But, when the direction of the axes and the magnitude of the indices are being determined, the crystal is immersed in a flat drop of a liquid whose refractive index is the same as that of the crystal in that particular vibration direction. Thus the wave-front travels through the crystal without the slightest deviation whatever its external shape. It is worth while to remember that on a universal stage this condition is not fulfilled, the refractive index of the hemispheres and other accessories being only near to that of the crystal.

It follows that the determination of the X and Z axes is free from errors involved in earlier steps; and the same applies to the Y axis, as it is simply the perpendicular to the plane defined by the other two.

Fig. 3 also shows the theoretical extinction direction curves for that particular mounting, drawn after the orientation of the axes and the values of the refractive indices had been found. As Professor Bernal has pointed out, they are the locus of the points of contact between the constant refractive index curves and a great circle rotating about the crystal's rotation axis. They are given here only for the purpose of comparison; the corresponding formulae and mathematical considerations will appear in another paper.

The difference between the theoretical and the experimental curves is not important as the X and Z axes are determined in optimum conditions, as explained above. That difference may be decreased if during the determination of the extinction directions the crystal is immersed in a liquid of refractive index near to the expected mean refractive index of the crystal; but it is not necessary, in general, to do so.

Uniaxial crystals.

The same general considerations apply, but the stereogram is much simpler. For every position of the crystal, one of the extinction directions is a vector lying in the equator of the indicatrix. As a result, a great circle appears in the stereographic projection, and its pole gives the direction of the axis (fig. 4).

The actual procedure is this: the stereogram of the extinction directions is drawn in order to get some idea of the orientation of the equator (only a few points are necessary). Next, the value of ω is determined and at the same time the position of the equator is defined, as the wave-fronts are now travelling without deviation. The pole of this great circle is drawn on the stereogram, and the axis found thereby is brought into the horizontal plane to measure ϵ.

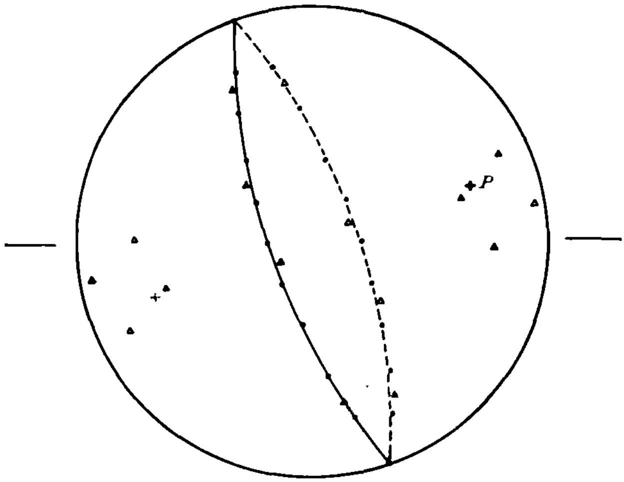

FIG. 4. Extinction directions in a uniaxial crystal. The triangles represent points obtained with the crystal rotating in air. The circles represent points obtained with the crystal rotating in a liquid of refractive index equal to ω. Also the equator and its pole P are shown.

Discussion of the results.

The value of the refractive indices obtained are as accurate as in any other immersion method, better results being obtained with monochromatic light, stabilized temperature, &c. The same applies to the optic angle calculated from these indices.

For the accuracy of the direction of the axes of the indicatrix there is a substantial difference between uniaxial and biaxial crystals.

In uniaxial crystals the errors are only those introduced by the mechanical behaviour of the goniometer and those due to the use of the stereographic net. So, it is easy to find the orientation of the indicatrix within $\frac{1}{2}^{\circ}$, the only condition being that the extinction directions should be observable.

In biaxial crystals the situation is different. Since the direction of the Z (or X) axis is determined as the direction of maximum (or minimum) refractive index, the accuracy depends on the rate of change of the observed index when the crystal is rotated. Consequently, the accuracy becomes greater, the greater the value of $\gamma-\beta$ ($\beta-\alpha$ in a negative crystal).

As an example of a biaxial crystal, the indices of the crystal of sodium-thyroxine-*dl* are: α 1·65, β 1·69, γ 1·79 (sufficient accuracy for the particular crystal structure work). Thus, $\gamma-\beta = 0{\cdot}10$. And it was possible to find the orientation of the Z axis within an error less than 1°, probably about ½°. The error in the orientation of the X axis is not more than 1°. As a result for the Y axis the error is also of the order of 1°. Certainly, this degree of accuracy is due to the very high birefringence of the crystal.

The method is sufficiently accurate for most purposes if

$$\gamma-\beta \text{ (or } \beta-\alpha) > 0{\cdot}04\,;$$

and becomes accurate to about $\pm 1°$ if

$$\gamma-\beta \text{ (or } \beta-\alpha) > 0{\cdot}06\,;$$

these conditions are rather elastic and the accuracy increases with increasing values of the difference.

If, by chance, or after trial, the Y axis of the indicatrix is nearly parallel to the axis of rotation of the crystal, in the above conditions $\gamma-\beta$ (or $\beta-\alpha$) may be changed into $\gamma-\alpha$. This will make much wider the field of application, and increase the accuracy.

For uniaxial crystals, as already explained, the accuracy is independent of the birefringence.

Conclusion.

The method described has the advantage that no expensive instruments are needed; it only requires one crystal, whatever its habit may be; and it gives both the orientation and magnitude of the indicatrix at the same time. Its main characteristic is that the crystal is rotated in the liquid till in a given vibration direction its index is found to be equal to that of the liquid. This saves many changes of liquid, as has to be done when fixed crystals are in random positions on a glass slide (usual method of dealing with triclinic crystals). As already pointed out, it is a great help for relating the optical directions to crystallographic directions, and may save time in the setting of crystals for X-ray diffraction, particularly uniaxial and orthorhombic ones. For this purpose it may be used in combination with any of the X-ray methods for setting crystals described by Hendershot,[1] Weisz and Cole,[2] and Jeffery.[3]

[1] O. P. Hendershot, Rev. Sci. Instruments (Amer. Physical Soc.), 1937, vol. 8, p. 436.

[2] O. Weisz and W. F. Cole, Journ. Sci. Instruments, London, 1948, vol. 25, p. 213.

[3] J. W. Jeffery, Acta Cryst. Cambridge, 1949, vol. 2, p. 15. [M.A. 10–525.]

I wish to thank Dr. W. Campbell-Smith, C.B.E., Keeper of Minerals in the Natural History Museum, and Dr. F. A. Bannister (Natural History Museum) for valuable help and encouragement; and most especially Professor J. D. Bernal, under whose direction my X-ray crystal analysis work is being done, and to whom I am deeply indebted for advice in the revision of this paper.