

Similarly in the determination of the isoelectric point with the multivalent ions Al^{+++} and Th^{++++} the amount of gas bound by the capillary plays a predominant part. Since it appears to be very difficult to reproduce this gas amount exactly, ζ also is subject to alterations and consequently the electrolyte concentration at which reversion of charge takes place. At the same time care should be taken that the amount of adsorbed gas on the capillary is in equilibrium with the amount of oxygen in the solutions which are used.

Testing of the law of VON SMOLUCHOWSKI²⁾ was done as follows: The platinum capillary was replaced by a Jena glass filter 7N4. We imitated the wall conduction with two platinized platinum plates on either side of the filter, between which was a resistance box. The platinum plates were made into unpolarizable electrodes by taking $10^{-4} n$ HCl + 0.1 % quinhydrone as filling. With this arrangement the formula of VON SMOLUCHOWSKI appears to be applicable, within the experimental error (1 %), to an area of "wall conduction" of 400—100,000 Ω .

Utrecht, April 1937.

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Chemistry. — *On the Possibility of Distinguishing Right- and Left-handed Structures in Crystals by means of their LAUE-Patterns.* By J. TER BERG and F. M. JAEGER.

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§ 1. In the chemical and crystallographical literature of to-day often still the opinion is held that, — according to FRIEDEL's principle¹⁾ of the superimposing of a centre of symmetry on the true symmetry of the crystal, when the latter is radiated through by X-rays, — it is in general impossible to distinguish the dextro- and the levogyatory crystals of optically active substances from each other by means of the LAUE-patterns obtained with them.

As a general rule this, of course, is true; however, in some particular cases there are exceptions to this rule and it is possible, by a suitable arrangement of the experimental conditions, yet to distinguish the right- and left-handed structures in this way. A general review of the problem, therefore, seems to be not out of place and is the aim of the present paper.

From FRIEDEL's principle the particular symmetry of the LAUE-pattern, obtained by means of a pencil of X-rays penetrating a crystal in a direction parallel to an axis of symmetry of the crystal, can in each case be predicted, if the proper symmetry of the crystal-species investigated and

¹⁾ G. FRIEDEL, *Compt. rend. Paris*, **157**, 1533, (1913).

the orientation of the photographic plate and the crystal with respect to the primary X-ray are accurately known. The results of the study of such LAUE-patterns have, — in all cases where the mutual orientation of plate and crystal were, indeed, faultless, — fully corroborated the exactness of those theoretical deductions¹⁾. Thus, for instance, it was stated, that the special distribution of the intensities of the diffraction-spots in the LAUE-patterns of uniaxial crystals, obtained by radiating through plan-parallel plates cut parallel to {001} or {0001} of such crystals, manifested the lack of symmetry with respect to definite planes perpendicular to the photographic film, if only the crystal did *not* possess either such planes of symmetry, or symmetry-axes of *even* period perpendicular to the direction of the principal binary, ternary, quaternary or senary axis. For this reason *dolomite* and *phenakite* [symmetry *): $A_3 \cdot C$ (also \bar{A}_6)]; *apatite* [symmetry: $A_6 \cdot \Sigma \cdot C$]; *nephelite* [symmetry: A_6]; *scheelite* and *erythrite* [symmetry: $A_4 \cdot \Sigma \cdot C$]; *wulfenite* [symmetry: A_4]; etc. all yielded LAUE-patterns on the basal face, the intensity-distribution of which proved only to have a single trigonal, hexagonal or tetragonal axis; and the same was stated in the case of *monoclinic* crystals, if radiated through in a direction perpendicular to {010}. On the other hand, a basal LAUE-pattern of *NiSO₄ + 6H₂O* [symmetry: $A_4 \cdot 2A_2' \cdot 2A_2''$]; of *quarz* and *cinnabar* [symmetry: $A_3 \cdot 3A_2$]; of *antimonylbariumtartrate + KNO₃* [symmetry: $A_6 \cdot 3A_2' \cdot 3A_2''$], yielded images of this kind, which proved to be symmetrical with respect to 2×2 ; 3; or 2×3 planes passing through the principal axis A_4 , A_3 or A_6 respectively.

Optically active substances which crystallize in one of the eleven²⁾ axially symmetrical classes: C_1 — C_6 ; D_2 — D_6 ; T and K , — will, therefore, in most cases yield LAUE-patterns which cannot be distinguished from their mirror-images, if the crystals are radiated through in a direction perpendicular to one or more symmetry-axes of even periods. More especially this holds for the crystals of the dihedral groups: D_2 , D_3 , D_4 and D_6 , — as these all possess binary axes perpendicular to their principal axis A_n , — if they are radiated through in the direction of this principal axis. The same is true for crystals of the classes T and O , if the pencil of X-rays traverses the crystals in the direction of their binary (\perp {100}; {110}) or quaternary (\perp {100}) axes. But an exclusively axial symmetry of the LAUE-pattern with crystals of one of the eleven classes mentioned will certainly appear in all cases, where *no* symmetry-axes of even period

¹⁾ F. M. JAEGER, *Proceed. R. Acad. Sc. Amsterdam*, **17**, 1204, (1915); H. HAGA and F. M. JAEGER, *ibid.*, **18**, 542, 1201, 1350, (1916).

*) The symbols used are: A_n = principal axis of period $\frac{2\pi}{n}$; A_2' or A_2'' are binary axes of two alternating sets; Σ is the principal plane of symmetry, perpendicular to A_n ; C = symmetry-centre.

²⁾ F. M. JAEGER, *Principle of Symmetry*, 2nd Ed., (1920), 81.

are present perpendicular to the direction of the pencil of X -rays used in the experiment. Thus, for instance, such a dissymmetry of the intensity-distribution of the diffraction-spots will certainly be observed with plan-parallel plates cut perpendicular to the principal axis of the classes: C_1 , C_2 , C_3 , C_4 and C_6 and also in class D_3 for a plate perpendicular to its polary binary axes or in the classes: T and O for plates cut parallel to $\{111\}$. Although in the class K_H of the cubic system no optically active substances will crystallize, it is worth while to remark here that also in this class plates cut parallel to $\{111\}$ will show this dissymmetry of their trigonally symmetrical LAUE-patterns. The facts mentioned were demonstrated in several cases; for instance, in the case of quartz¹⁾ $\perp \{1\bar{2}10\}$ (normal pattern, Plate IV, fig. 13), in class K_H for ferric ammonium-, and chromic potassium alum²⁾ $\perp \{111\}$ (Plate IV, figs. 2 and 3): furthermore for sodium chlorate $\perp \{111\}$ and doubtlessly it will also be found with substances such as cuprite, ammonium chloride, SCHLIPPE's salt, and the nitrates of Ba, Sr, Pb; etc.

On the other hand, the basal LAUE-patterns of d - and l - $\{Co(Ene)_3\}Br_3 + H_2O$ proved to be identical, — as might have been expected, because here there are two sets of binary axes present perpendicular to the tetragonal axis A_4 .

§ 2. Now let us consider such simple cases as, for instance, the basal images in the classes C_1 — C_6 with their unique symmetry-axes (polar) or that of non-polar apatite [symmetry $A_6 \cdot \Sigma \cdot C$], radiated through in the direction of the principal axis.

If the X -ray source and the photographic plate be kept in an unchanged and identical position, but in two successive experiments the crystal is turned through 180° round a direction \perp principal axis, — so that in the first experiment the one and in the second experiment the other end of the principal axis points towards the luminous source, — then the two LAUE-patterns obtained on the same side of the photographic film will prove to be each other's mirror-images and, — as long as they are moved in their own plane only, — they cannot be brought to coincidence with each other. The question as to whether the one or the other end of the principal axis points towards the X -ray focus (or towards the photographic film) is, of course, of particular interest in those cases where A_n is a polar axis, because now the two ends are non-equivalent; so that, when the morphological development of the terminal crystal-facets at both ends of the axis clearly proves to be different (hemimorphic habitus), or when the said non-equivalence of the two poles can in some other way (thermo- or piezo-electrical phenomena, figures of corrosion;

¹⁾ H. HAGA and F. M. JAEGER, loco cit., 549.

²⁾ Idem, 17, 1204, (1915).

etc.) easily be stated, the fact mentioned above may be used in the case of dextro- and levogyrotory substances for distinguishing between the one and the other spatial configuration. For if, for instance, the crystals of the two antipodes in the two successive experiments indicated above be placed between the X -ray source and the photographic film in exactly the same position, — i.e. in both cases either with their analogous or with their antilogous poles towards the luminous source, — then the obtained LAUE-patterns will, in each of the two cases mentioned, manifest a truly non-superimposable intensity-dissymmetry of their spot-distribution and thus appear as planar mirror-images of each other.

In this connection still another remark can be made: if the pencil of X -rays does not traverse the optically active crystal along a symmetry-axis, but in some direction including with it an arbitrary angle α ($< 90^\circ$), the LAUE-pattern obtained will, of course, appear distorted and, therefore, be quite unsymmetrical. But if the experiment, under the same rigorous conditions as emphasized in the above, first be made with a crystal of the dextrogyrotory component and subsequently with a crystal of the levogyrotory substance, — the angle α being in the two cases kept exactly the same, — the unsymmetrical LAUE-pattern I also will prove to be the planar "mirror-image" of II . In this way, the d and l -crystals in each case can, therefore, also be distinguished from each other with certainty, — although, of course, this latter method will, in general, practically be of no great significance.

More particularly where the question may arise whether isomorphous, analogously constituted optically active compounds of different directions of rotation possess analogous or antilogous spatial configurations, the experiments of this kind can, without any other chemical or optical investigations, bring a final decision.

§ 3. As an example of this, we here will deal with the case of the optically active, isomorphous complex salts of the type: $\{Me^{III}(Base'')_3\}X_3$, in which $Base'' = d$ - or l - $Chxn$ (= cyclohexane-trans-1-2-diamine) and Me^{III} are Co, Cr or Rh, — which metals can in these salts substitute each other in a rigorously isomorphous way. It is true, — the mutual spatial configurations of these salts can be and have been established in a number of other ways, — either by the study of their rotatory dispersion, by that of the solubilities of their derivatives with a similar optically active substance or by means of DÉLÉPINE's method of the so-called "optically active racemates"¹⁾. But it is of interest to show that perfectly agreeing results also can be obtained by means of a simple study of the LAUE-patterns of these salts.

The isomorphous salts under consideration crystallize with $3H_2O$

¹⁾ Cf. F. M. JAEGER, these Proc., 40, 3, 108, (1937); Nachrichten Ges. d. Wiss. Göttingen, N. F. 1, 199, (1937); Bull. Soc. chim. franç., (5), 4, (1937).

(*Cr*, *Rh*) or with $4H_2O$ (*Co*) and they all have quite comparable crystal-forms. They are *hexagonal-pyramidal* (class C_6) and have a typical *hemimorphic* habitus: $p = \{10\bar{1}1\}$, predominant; $\omega = \{10\bar{1}\bar{1}\}$, narrow; $c' = \{000\bar{1}\}$, large and lustrous; $c = \{0001\}$ often absent, but, when present, only very small, — much smaller than c' . The polarity of the principal axis, therefore, is here immediately recognizable and the two ends of it can in each case be readily distinguished and identified¹⁾.

Of the *dextrogyratory* salts, all containing 3 molecules of *l-Chxn* within their complex ions, LAUE-patterns were made in such a way that the pencil of X-rays (*tungsten-anticathode*; $V = 35000$ Volts) always went along the senary axis in the direction from $\{000\bar{1}\}$ towards $\{0001\}$; the distance of the crystal from the photographic film, — of which the side used was beforehand clearly marked, so that after development it could always easily be recognized, — was 5 c.M.

In this way, successively, LAUE-patterns of the *cobaltum*, the *chromium* and the *rhodium* salts were prepared; they are reproduced in the Fig. 1—3.

From these figures it is easily seen that the dissymmetry of the intensity-distribution of the spots has in all three cases exactly *the same character*, — thus proving that the spatial configuration of the molecules, as well as that of the content of the elementary cells of these crystals (6 molecules pro cell; senary screw-axis), is for all of them just *the same*.

As a consequence of the much greater diffractive power of the *Rh*-atoms in comparison with that of the *Co*- or *Cr*-atoms, the pattern in Fig. 3 shows a somewhat other aspect than those in Fig. 1 and 2; but notwithstanding this, the analogy in their character still is easily recognized, — more particularly by taking into account those diffraction-spots with the same symbols $\{hkl\}$ which show strongly deviating intensities.

Especially in cases where the crystals investigated have a polar axis, the application of this method, — if the necessary conditions of orientation be strictly fulfilled, — may be considered to be perfectly safe.

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¹⁾ F. M. JAEGER and L. BIJKERK, these Proceed., 40, 12, 116, 246, 316, (1937).

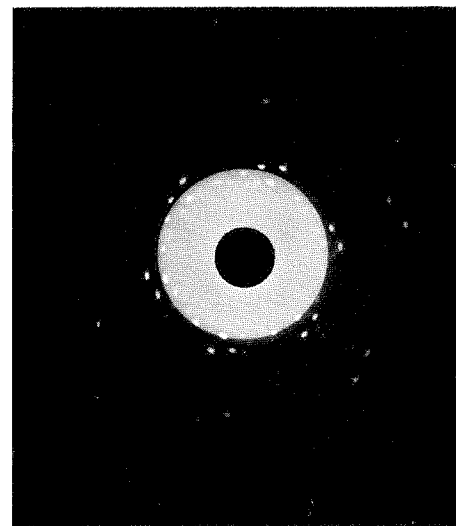


Fig. 1. LAUE-pattern of $D\text{-}\{Co(l\text{-}Chxn)_3\}Cl_3 + 4H_2O$ perpendicular to $\{0001\}$.

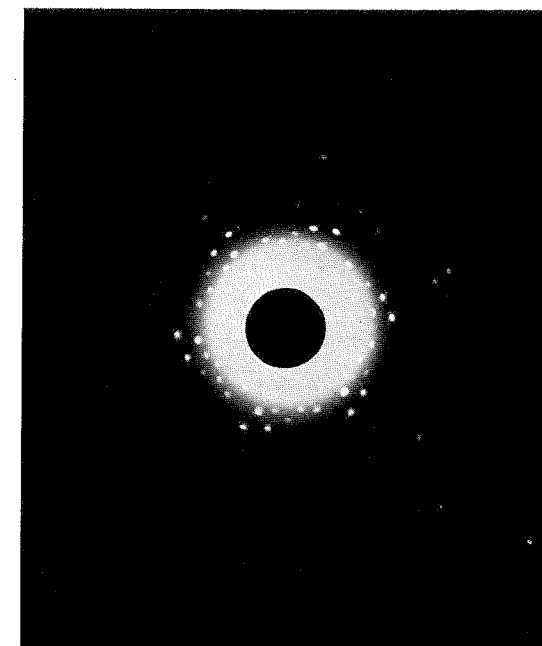


Fig. 2. LAUE-pattern of $D\text{-}\{Cr(l\text{-}Chxn)_3\} + 3H_2O$ perpendicular to $\{0001\}$.

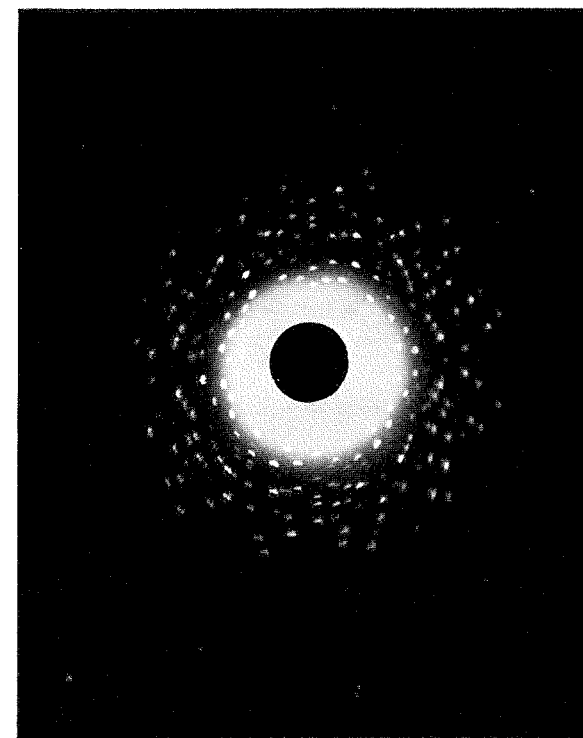


Fig. 3. LAUE-pattern of $D\text{-}\{Rh(l\text{-}Chxn)_3\} + 3H_2O$ perpendicular to $\{0001\}$.