

NOTE ON THE LAUE SYMMETRY EXHIBITED
BY ORTHOGONAL CRYSTALS

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In the Laue method of *x*-ray analysis the most useful photographs are those taken with the beam along the direction of the principal axis or inclined thereto by a few degrees. Consequently, in the case of orthogonal crystals (i.e., orthorhombic, tetragonal, cubic, trigonal, and hexagonal), we are more familiar with the appearance of the diagrams so obtained than we are for those resulting from the beam directed at right angles to this axis and along a lateral (*a* or *b*) axis, except, of course, in the case of cubic crystals. The pictures obtained with the latter settings, however, are sometimes of very great importance. For example, Laue photographs with the beam along the *a* and *b* (orthohexagonal) axes are useful for distinguishing between members of certain pairs of space groups in the rhombohedral division of the hexagonal system.¹

The object of the present paper is to draw attention to the symmetry exhibited by Laue diagrams of crystals which are characterized by a two-, three-, four-, or six-fold symmetry axis and planes of symmetry containing this axis, but having no plane of simple symmetry normal to it. They may possess two-fold axes perpendicular to the principal axis and not contained in the symmetry planes. The presence or absence of other elements of symmetry does not concern us at present.

There are seven crystal classes which have to be considered, namely C_2^v , C_4^v , D_2^d , T^d , C_3^v , D_3^d , C_6^v .²

But in the Laue method, since a center of symmetry is automatically introduced by Friedel's Law due to the inability of the method to distinguish between the parallel planes (*hkl*) and ($\bar{h}\bar{k}\bar{l}$), other classes show the same Laue symmetry as those enumerated above. They may be grouped together as follows: V , C_2^v , V^h ; C_4^v , D_2^d , D_4 , D_4^h ; C_3^v , D_3 , D_3^d ; C_6^v , D_3^h , D_6 , D_6^h ; T^d , O , O^h .

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¹ Barnes, W. H., and Wendling, A. V., *Trans. Roy. Soc. (Canada)*, vol. 27, Sect. 3, pp. 133-140, 1933.

² For brevity classes will be referred to by symbols. For corresponding names, see Wyckoff, R. W. G., *Analytical Expression of the Results of the Theory of Space Groups*, Carnegie pub. 318, Table 1, p. 16, Washington, 1930, or Wyckoff, R. W. G., *The Structure of Crystals*, 2nd Ed., Table 1, pp. 22, 23, Chem. Cat. Co., 1931.

Of these five groups of classes, four exhibit the Laue symmetry of holohedral classes, namely, V^h , D_4^h , D_6^h , O^h . In the Laue method all classes in these four groups appear to possess a plane of symmetry normal to the principal axis and planes of symmetry containing this axis whether or not such planes are actually present in the crystal. In Laue diagrams the fifth group of classes, showing the Laue symmetry of D_3^d , exhibits only planes of symmetry containing the principal axis and no symmetry plane normal to this axis.

Unless this is recognized some confusion may arise in practice when Laue photographs are obtained of crystals belonging to the classes under discussion. For example in Figure 2 the diagram for tourmaline (C_3^v) with the beam along the b (orthohexagonal) axis is not symmetrical about the trace of the plane normal to the c axis. It appears to be set incorrectly about an axis perpendicular to the c axis and parallel to the diagram. Actually the photograph in Figure 2 was obtained as follows. A slip of tourmaline was polished with plane parallel sides of area much larger than the cross-sectional area of the x -ray beam. The plane of the polished surfaces coincided with the $(10\bar{1}0)$ plane to within 10 and 15 minutes of arc, respectively, in the prism zone and in the zone normal to the prism. The crystal slip was set optically so that the $(10\bar{1}0)$ plane was normal to the direction of the x -ray beam. The beam, therefore, coincided almost exactly with the b (orthohexagonal) axis so that the crystal was set correctly.

That the symmetry of the diagram obtained, namely, only about the trace of the symmetry plane $(11\bar{2}0)$, is that which should be expected is clear from the following argument.

In Figure 1(A), $\bar{a}Oa$, $\bar{b}Ob$, $\bar{c}Oc$ are three straight lines intersecting at O and making angles of 90° with one another.

The figure $MNPQRS$ is drawn as a regular bipyramid to avoid unnecessary complications. In the general case each of the points at the corners should consist of four points so that the indices of the faces will be (hkl) , $(\bar{h}kl)$, $(h\bar{k}l)$, $(\bar{h}\bar{k}l)$, $(hk\bar{l})$, $(\bar{h}k\bar{l})$, $(h\bar{k}\bar{l})$, $(\bar{h}\bar{k}\bar{l})$, where h , k , and l have different values in each set of indices.

Now since the Laue method makes O a centre of symmetry the faces NRS , QRS , QPS and NPS appear to be equivalent to the faces QPM , NPM , NRM and QRM , respectively. . . 1.

In tourmaline, $\bar{a}Oa$, $\bar{b}Ob$, $\bar{c}Oc$ are the directions of the a , b , c ,

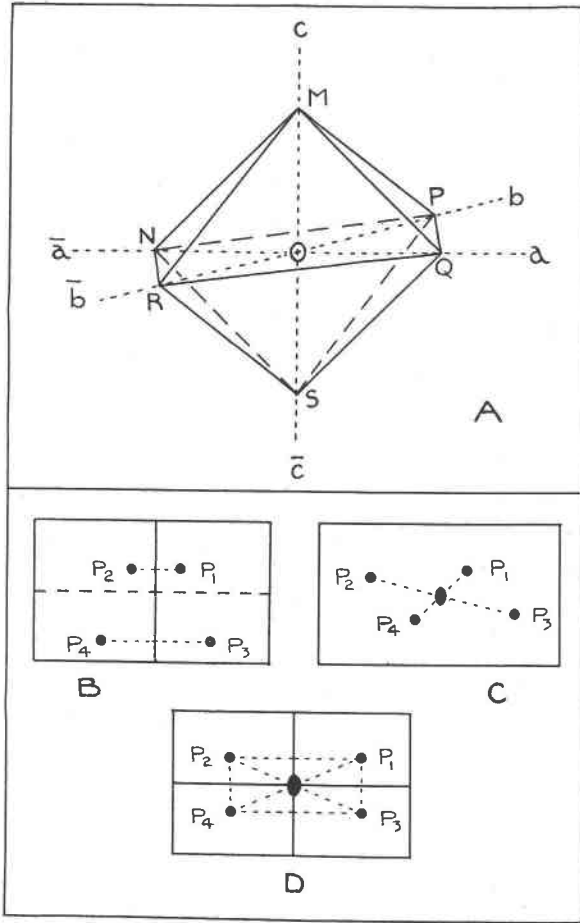


Fig. 1

axes, respectively, in orthohexagonal co-ordinates, and $MRSP$ is a plane of symmetry.³

Therefore the faces QPM , QRM , QPS and QRS are equivalent to the faces NPM , NRM , NPS and NRS , respectively. . . 2.

Combining data 1 and 2, the faces QPM , NPM , QRS and NRS are equivalent to each other, the faces QRM , NRM , NPS and QPS are equivalent to each other, but these two sets of faces are not

³ Barnes, W. H., and Wendling, A. V., *Trans. Roy. Soc. (Canada)* vol. 27, Sect. 3, pp. 169-175, 1933.

mutually equivalent. Hence $QPNR$ does not appear as a plane of symmetry. It will be noted that $\bar{a}Oa$ becomes a two-fold axis of symmetry, because a rotation of the figure through an angle of 90° about $\bar{a}Oa$ as axis brings the mutually equivalent faces NPM and QPM into coincidence with the equivalent pair of faces NRS and QRS , respectively, and the mutually equivalent faces NRM and QRM into coincidence with the faces NPS and QPS , respectively, to which they are equivalent. Thus the class C_3^v possesses the Laue symmetry of D_3^d .

The general type of symmetry to be expected, therefore, in a Laue diagram obtained with the beam along the direction $\bar{b}Ob$ which lies in the symmetry plane $MRSP$ is shown diagrammatically in Figure 1(B). The points P_1, P_2, P_3, P_4 arise from the general pairs of planes $(h\bar{k}l), (\bar{h}k\bar{l}); (\bar{h}k\bar{l}), (h\bar{k}l); (h_1\bar{k}_1\bar{l}_1), (\bar{h}_1k_1l_1); (h_1k_1l_1), (\bar{h}_1\bar{k}_1\bar{l}_1)$, respectively, where h, k and l have not the same values as h_1, k_1 and l_1 , respectively. The diagram is symmetrical only about the trace of the plane $MRSP$, shown as a full line in Figure 1(B).

Similarly, since $\bar{a}Oa$ appears to be a two-fold axis of symmetry the type of Laue diagram obtained with the beam along this axis may be represented diagrammatically as in Figure 1(C) where the points P_1, P_2, P_3, P_4 arise from the general pairs of planes $(\bar{h}k\bar{l}), (h\bar{k}l); (\bar{h}_1k_1\bar{l}_1), (h_1\bar{k}_1\bar{l}_1); (\bar{h}_1\bar{k}_1\bar{l}_1), (h_1k_1l_1); (\bar{h}k\bar{l}), (h\bar{k}l)$, respectively, where h, k and l have not the same values as h_1, k_1 and l_1 , respectively. The diagram exhibits only the trace of the two-fold axis normal to the diagram shown as an ellipse at the centre, and consequently possesses only a centre of symmetry.

The same types of diagrams are obtained from the classes D_3 and D_3^d since both of these also possess the Laue symmetry of D_3^d .

As mentioned above the other four groups of classes under examination exhibit Laue symmetry elements which make the plane $QPNR$ appear as a plane of symmetry in addition to the plane $MRSP$. It will be seen that this makes the two sets of faces 1 and 2 mutually equivalent, so that $QMNS$ also is a plane of symmetry, and the Laue diagram with the beam along $\bar{a}Oa$ or along $\bar{b}Ob$ will have the general appearance shown in Figure 1(D). It is symmetrical about the traces of the planes $QPNR$ and $MRSP$ (shown by full lines) which intersect in the trace of the two-fold axis $\bar{a}Oa$ (or $\bar{b}Ob$) which is shown as an ellipse. It is symmetrical, therefore, about two lines at right angles intersecting in a centre of symmetry.

The points P_1, P_2, P_3, P_4 arise from the four pairs of the eight sets of planes constituting the general form $\{hkl\}$, where h, k and l have the same values, respectively, in each set of planes of the form. In the special case of the classes having the Laue symmetry of the class O^h when $\bar{a}Oa$ (or $\bar{b}Ob$) appears as a four-fold axis the distances P_1P_3, P_1P_2, P_2P_4 and P_3P_4 in Figure 1(D) are all equal when the beam is along this axis.

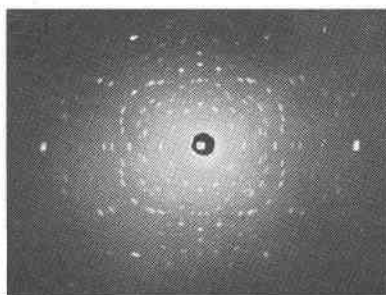
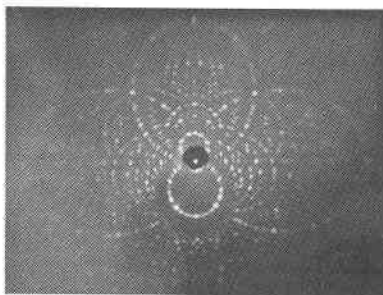


FIG. 2. Tourmaline. Beam \perp to $(10\bar{1}0)$

FIG. 3. Calamine (Hemimorphite).
Beam \perp to (010)

Figure 3 shows the Laue diagram obtained for calamine (hemimorphite), class C_{2v} , with the beam along a b axis. The diagram has the symmetry characteristics of Figure 1(D).

The importance of recognizing the symmetry to be expected from Laue diagrams obtained with the beam along a lateral axis in the case of crystals belonging to the classes C_{3v} , D_3 , and D_{3d} is due to the fact that, according to the symmetry exhibited, the space groups $C_{3v}^1, C_{3v}^3, D_3^2, D_3^4, D_3^6, D_{3d}^3, D_{3d}^4$ may readily be distinguished from $C_{3v}^2, C_{3v}^4, D_3^1, D_3^3, D_3^5, D_{3d}^1, D_{3d}^2$, respectively. In the former, a axes coincide with two-fold axes of rotation and b (orthohexagonal) axes lie in symmetry planes perpendicular to $\{0001\}$, while, in the latter set, b axes coincide with two-fold axes and a axes lie in symmetry planes perpendicular to $\{0001\}$.

The following experimental procedure, therefore, will allow a rapid and correct choice of space group to be made between the two members of each of these seven pairs.

The possible space groups are reduced to one of these pairs by the usual methods.⁴ The crystal is then mounted on a spectro-

⁴ For example see Astbury, W. T., and Yardley, K., *Trans. Roy. Soc. (London)*, vol. 224A, p. 221, 1924.

graph equipped with goniometric arcs and a Laue photograph is taken with the x -ray beam along the c axis. The positions of the a and b axes in this picture are readily identified by simple visual inspection. The position of the crystal is altered so as to make one of these axes (say an a axis) coincide with the axis of rotation, leaving the c axis along the direction of the beam. The crystal is rotated through an angle of 90° about the axis of rotation which, in this case, places a b axis in coincidence with the direction of the beam. A Laue photograph is taken with the crystal in this position (i.e., b axis along the beam, a axis along axis of rotation). Finally, the crystal is rotated on the arcs through 30° about the c axis, which is parallel to the plane of the photographic plate. This brings a b axis into the axis of rotation and an a axis along the direction of the beam. A third Laue photograph is taken with this setting (i.e., a axis along the beam, b axis along axis of rotation).

If there is any doubt as to which axis (a or b) is along the axis of rotation in the last two settings an oscillation or complete rotation photograph for each setting will allow a decision to be made because the primitive translations (a_0 and b_0) along the a and b axes are related in such a way that $b_0 = a_0\sqrt{3}$.

From the Laue diagrams obtained with the beam along the a and b axes, respectively, visual examination will show immediately if the a axis appears as a two-fold axis (Figure 1(C)) and the b axis as lying in a plane of symmetry (Figure 1(B) turned through 90° about an axis normal to plane of paper since the c axis will be horizontal) or vice versa. If the former then the space group is C_{3v}^1 , C_{3v}^3 , D_3^2 , D_3^4 , D_3^6 , D_{3d}^3 , or D_{3d}^4 . If the b axes are two-fold axes and the a axes lie in symmetry planes in the Laue diagrams then the space group is the alternative C_{3v}^2 , C_{3v}^4 , D_3^1 , D_3^3 , D_3^5 , D_{3d}^1 , or D_{3d}^2 , respectively.

In conclusion some observations by Hägg⁵ on crystals of potassium and rubidium dithionate are of interest. He notes in his paper that both the potassium and rubidium salts show the Laue symmetry D_3^d but only clearly in the photographs of the former. In the case of the latter the diagram along the three-fold axis has the symmetry of D_6^h while that along the two-fold axis is said to agree with D_3^d . The reproduction of his photograph for rubidium dithionate with the beam along a two-fold (a) axis, however, is symmetrical about two lines at right angles inter-

⁵ Hägg, G., *Zeit. Krist.*, vol. 83, pp. 265-273, 1932.

secting in a centre of symmetry as in Figure 1(D). Such a diagram is not compatible with D_3^d .

Work which we have been carrying out on the dithionates has been hampered very much by the prevalence of twinning. The rubidium salt apparently has a much greater tendency towards twin formation than has the potassium dithionate because, although we have been able to isolate only one crystal of the latter exhibiting the Laue symmetry of D_6^h , we have only obtained one specimen of the former which shows the Laue symmetry of D_3^d . In this case, however, the symmetry of D_3^d was exhibited by the diagrams with the beam along both the two-fold (a) and three-fold (c) axes. In view of this result it appears that Hägg's crystal of rubidium dithionate may have been twinned.

We are indebted to Dr. R. P. D. Graham, Professor of Mineralogy, for excellent single crystal specimens of calamine (C_2^v), chalcopyrite (D_2^d), tourmaline (C_3^v), calcite (D_3^d), greenockite (C_6^v), and tetrahedrite (T^d) all of which showed the Laue symmetry to be expected of their respective classes. We are also indebted to Dr. F. F. Osborne, Assistant Professor of Geology, for his supervision of the grinding and polishing of the tourmaline slip mentioned above.