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A New Aid to the Determination of the Point-Group Symmetry of Transparent Crystals

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The patterns formed by electrical breakdown paths provide a new way to investigate the point-group symmetry of transparent crystals because the paths lie along equivalent directions. A point-group is uniquely determined from the observation in a single-crystal slice of non-degenerate breakdown configurations. Such non-degenerate configurations are formed in most monoclinic and in all triclinic crystals, while most crystals of higher symmetry reveal degenerate configurations which are compatible with more than one point group. Degeneracy, however, is not an inherent property of the breakdown process and might be removed by suitable techniques. Since the paths are believed to be formed by electron avalanches, the symmetry shown by the breakdown pattern probably refers to the symmetry of the electrical fields within the crystal that influence the motion of electrons. The symmetry of the breakdown pattern is usually identical with the symmetry of the crystal determined by other methods. A new test for the lack of centrosymmetry in transparent crystals is described.

Introduction

This paper introduces the study of the patterns formed by electrical breakdown paths as a new aid to the determination of the point-group symmetry of transparent crystals. Each crystal shows an overall breakdown pattern that conforms with one or more point-group symmetries. Individual breakdown patterns, consisting of paths that lie along equivalent directions of the crystal, are called here breakdown configurations. Each configuration conforms with the symmetry of the overall pattern, but may differ from other configurations in orientation and in number of paths. Since the paths are believed to be formed by electron avalanches, the symmetry revealed by the pattern is probably the symmetry of the electrical fields within the crystal that influence the motion of electrons. Although, for crystals of high symmetry, the method suffers from the same limitations that are encountered in morphological studies, in that 'special forms' (here called degenerate configurations*) tend to develop, it is

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* A degenerate electrical breakdown path configuration is one that consists of paths that lie in planes or along axes that could be symmetry operators. When the paths are in such positions it is not possible to determine whether or not the planes or axes are symmetry operators for the breakdown process. Hence degenerate configurations are compatible with

sometimes possible to obtain less degenerate configurations, or non-degenerate configurations, by changing the conditions of breakdown, such as by changing the temperature of the crystal or by applying overvoltages. While the degeneracy is seldom completely removed, the partial information that is obtained is usually sufficient to show that certain point groups are incompatible with the pattern. The incompatible groups may have higher or lower symmetries than the true symmetry of the crystal for the breakdown process, depending upon the nature of the degeneracy. If one then gains knowledge by some other means of the existence of those symmetry elements which are not established by the degenerate configuration, or, if one obtains a non-degenerate breakdown configuration, a point-group symmetry is uniquely determined. Since the breakdown pattern lies in three dimensions, its full symmetry is revealed in a single-crystal section or slice. Thus euhedral crystals are not necessary for the symmetry determination.

The point-group symmetry is most simply determined by examining the breakdown configurations in

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two or more point-group symmetries. When all configurations are degenerate the overall pattern is degenerate and the point-group symmetry of the crystal for the breakdown process is not established.

crystal sections whose orientation corresponds with the reference orientation of the standard stereograms of point-group symmetry, since the breakdown configurations can then be directly compared with the stereograms. The procedure is the following: (1) breakdown configurations of the same polarity are obtained from each side of the section; (2) a polar plot is made of the surface projections of the paths. The paths that originate at the top surface of the section are represented by dots, while the paths that originate at the bottom surface are represented by circles. The breakdown path stereogram, so formed, can then be compared with the standard stereograms of point-group symmetry.

The test for centrosymmetry is made by determining whether or not the paths originating at the top surface of any section or slice lie parallel with those originating at the bottom surface. When the paths are not parallel the crystal lacks a center of symmetry for the breakdown process. When the paths are parallel either the crystal has a center of symmetry for the breakdown process, or the configuration is degenerate and the lack of a center of symmetry for the process does not appear. However, there seems to be a limit to the sensitivity of the breakdown paths to determine the symmetry of crystals, since the non-degenerate breakdown pattern obtained in colemanite (see below) seems to show a center of symmetry, whereas other tests indicate that it lacks a center.

The experimental techniques for obtaining electrical breakdown paths are simple. It is desirable to produce only partial breakdown so that the paths are not destroyed by secondary effects. Thus pulsed voltage is used. A single pulse produces a configuration—not just a single path. A point–plane electrode system is used, with the crystal section, seed or slice surrounded by an insulating medium such as transformer oil. The crystal slice may be several millimetres thick in most cases, if voltages corresponding to air spark-gap distances of 2–3 in. are used. A pulse with a rise time of 10^{-6} sec. or faster is advisable, since for slower rise times there is a tendency for the spark to strike across the surface or for rupture breakdown to occur.* It is sometimes advantageous to stack a few glass plates between the crystal and the ground electrode so as to introduce a large series resistance. The configurations are either positive or negative, depending upon the sign of the voltage applied to the point electrode, and they are permanent. Thus the configurations can be viewed at any time by using above-stage illumination.

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* The paths considered in this report are 'partial breakdown paths'. They are electrical breakdown paths which originate at the point electrode and penetrate only part way through the crystal. Paths that penetrate completely through the crystal are 'rupture paths'. A rupture path is not necessarily an extended partial breakdown path, and it may be devoid of orientation. A tentative explanation is that the rupture path is sometimes due to a catastrophic liberation of electrons from the cathode, whereas the partial breakdown paths are formed from electrons already present in the crystal.

We may classify the study of electrical breakdown path patterns as an extension of the study of pure crystal morphology (i.e. without etch-figure studies) because any set of equivalent breakdown path directions $\langle uvw \rangle$ constitute the normals to the set of equivalent crystallographic planes $\{hkl\}$ given by $h = a_1R$, $k = a_2R$, $l = a_3R$, where $R = ua_1 + va_2 + wa_3$ is a breakdown path direction in real crystal space. From this point of view the study of the degenerate configurations in alkali halide crystals is equivalent to the study in pure crystal morphology of euhedral alkali halide crystals in the forms of the cube, the octahedron, the dodecahedron and various trisoctahedra, since these forms characterize the breakdown configurations in the alkali halides at various temperatures (Davisson, 1946, 1948a).

A few crystals are now known to yield non-degenerate patterns when minimum breakdown voltage is applied at room temperature. These are ADP, KDP, apatite and colemanite, which are described below. It will be shown, also, that the patterns of all triclinic and of most monoclinic dielectric crystals are non-degenerate. Thus a point group symmetry for the breakdown process can be uniquely determined for many more crystals, especially in the systems of lower symmetry.

Background

Electrical breakdown paths in distinct crystallographic orientation were first observed independently and almost simultaneously around 1930 by Inge & Walther (1930, 1931), von Hippel (1931a, 1932, 1934) and Lass (1931), who investigated the alkali halides, chiefly at room temperature. The paths were observed to lie along one or more of the sets of equivalent directions $\langle 100 \rangle$, $\langle 110 \rangle$ and $\langle 111 \rangle$ in the alkali halide series (von Hippel, 1931a, 1932, 1934). For NaCl, a dependence of orientation upon the polarity and gradient of the applied field, but not upon the orientation of the crystal section, was noted. By studying the breakdown configurations in barite, von Hippel (1931b) confirmed that the paths proceed in the same crystallographic directions in all sections of a given crystal. The existence of surface breakdown paths in the same crystallographic orientation as the volume paths was also observed by von Hippel (1931a, 1932, 1934), according to whom the speed at which breakdown develops classifies the process as an electronic phenomenon. Breakdown configurations, sometimes showing anomalous behavior, were reported by Kreft & Steinmetz (1937) and by Steinmetz (1934) for an assortment of minerals; but it is now believed that the anomalies are not real, since they have not been reproduced (Davisson, 1946, 1948a) and could be the result of an optical illusion if vertical rather than horizontal illumination was used to view the configurations. More recently the author observed that the orientation of the paths in the alkali halides is temperature dependent (Davisson, 1946, 1948a). By in-

vestigating a sequence of crystal structures ranging from ionic to covalent it also became apparent that (1) the orientation phenomenon was not dependent upon the type of bonding, and (2) the paths formed patterns whose symmetry was given by the macroscopic symmetry of the crystal (Davisson, 1946, 1948a). By studying the path configurations in non-centrosymmetrical crystals Davisson & Burstein (1951) then established that the breakdown patterns conform exactly with the point-group symmetry of crystals.

It seems probable that the mechanism of orientation of electrical breakdown paths involves the interaction of electron waves with the vibration spectrum of the crystal, as first conceived by von Hippel (1946) and then modified and developed theoretically by Offenbacher & Callen (1953). The paths, for example, are definitely not formed by any mechanical action, since configurations that are sensitive to temperature and polarity are formed in such crystals as ADP and $NaBrO_3$ (see below) which lack preferential mechanical properties such as cleavage. Further, such properties as (1) the rapidity at which the paths form (von Hippel, 1931a, 1932, 1934; von Hippel & Alger, 1949), (2) the absence of orientation in some crystals at low temperature (Davisson, 1946, 1948a), and (3) the sensitivity of the path orientation to the temperature of the crystal (Davisson, 1948a) would seem to rule out any orientation mechanism based upon melting or other thermal processes. While the existing theory appears to be basically correct, it is incomplete in several respects: it does not account for the existence of (a) star patterns in the alkali halide crystals, (b) orientated paths in molecular crystals such as sulphur (Davisson, 1948b, 1953, 1954), and (c) unidirectional paths in non-centrosymmetrical crystals* (Davisson & Burstein, 1951).

Analysis of breakdown patterns

ADP and KDP

According to Groth (1908, p. 795) ADP and KDP, $[(NH_4)H_2PO_4$ and $KH_2PO_4]$, crystallize in the tetragonal system. The crystal habit exhibits only the following forms: tetragonal prism {100} and tetragonal dipyramid {101}. The point-group symmetry, obtained from etch-figure studies, is given as $\bar{4}2m$. Owing to the simplicity of the habit, the point-group symmetry is not revealed by morphological studies.

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* The asymmetry that might be introduced into the electron-scattering mechanism by means of piezoelectric or electrostrictive forces is not adequate to account for the distinct difference between the positive and negative configurations in ADP and KDP unless break-down takes place by different mechanisms, such as by electrons and by holes, in the two cases; or, unless a space-charge field acts in conjunction with the applied field to materially alter the nature of the deformation with change of polarity. Burstein, in discussion, has suggested that the lack of a center in the breakdown configurations might be due to the mechanism of ionization where the sequence of inelastic collisions of electrons with atoms may be decisive.

We begin our study of electrical breakdown paths in ADP by selecting a crystal and considering its coordinates. We can locate the principal axis (the c axis) by inspection, but, since the a and b axes are equivalent in tetragonal crystals, we are unable to distinguish between the tetragonal prism faces (100) and (010). A difference between the a axis and the b axis in such crystals as ADP and KDP becomes apparent, however, when the breakdown configurations are considered. The configurations show that once a coordinate system is erected in one sample, the coordinate axes, but not their positive directions, are uniquely specified for all samples of ADP and KDP. This means that one can always distinguish a (100) face from a (010) face, but not from a $(\bar{1}00)$ face. We erect our coordinate system in such a way that the components of some of the paths in the normal negative breakdown configuration in ADP or KDP are all positive. To demonstrate that this construction leads to a unique set of axes let us consider the volume breakdown configuration, shown in Fig. 1, which is ob-
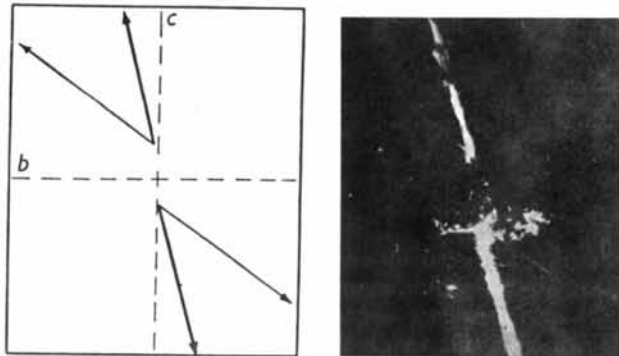

Fig. 1. Electrical breakdown path configuration in a $(\bar{1}00)$ section of ADP. This configuration shows reflectional symmetry across the {110} planes and twofold symmetry about the a axis. This information indicates that the point-group symmetry is $\bar{4}2m$. The two steep paths are enlarged owing to secondary effects attending rupture of the sample.

served in a slice cut parallel to a tetragonal prism face. We assume that the paths in a negative configuration are directed away from the point electrode and thus have positive normal components into the section. We adopt a right-handed set of axes and find that none of the paths has components that are all positive when the b axis is directed into the section, while some paths have components that are all positive when the a axis is directed into the section. Thus in Fig. 1, with the axes as shown, the paths with positive components lie in the upper left quadrant. This result is not changed if the direction of the c axis is reversed. It follows that the slice shown in Fig. 1 consists of the indistinguishable faces (100) and $(\bar{1}00)$ and not the faces (010) and $(0\bar{1}0)$. We are thus able to erect a unique set of coordinate axes for our ADP and KDP specimens, and will now consider the pattern in more detail (Davisson & Burstein, 1951).

In ($\bar{1}$00) sections, the negative ($\bar{1}$00) configuration, i.e. the half-pattern that is formed when a negative voltage is applied to the point electrode situated on the top surface of the ($\bar{1}$00) sections, consists of four paths which are contained within two diagonally situated quadrants, Fig. 1. Of the two paths in one quadrant one dips steeply, the other gently. In surface projection, the steep path lies much closer to the c axis than does the gentle path. The complete ($\bar{1}$00) configuration shows twofold rotational symmetry about the normal to the section, i.e. about the a axis. If we assume that all the paths are symmetrically equivalent and consider the possible symmetry elements of the tetragonal system, we can deduce from the ($\bar{1}$00) configuration (1) that the a axis shows twofold rotational symmetry; (2) that the (010) and (001) planes are not reflecting, since these reflections would send the paths into the unoccupied quadrants; and (3) that the (110) and (1$\bar{1}$0) planes are reflecting, since these reflections will account for the existence of two paths in each occupied quadrant and will also account for their difference in slope. The symmetry elements deduced from this configuration are sufficient, in this case, to suggest that the point-group symmetry of ADP is $\bar{4}$2m for the breakdown process, since this is the only point group of the tetragonal system that possesses the partial symmetry that is observed. In most cases, however, it is necessary to observe the whole individual pattern, i.e. the ($\bar{1}$00) configuration and the (100) configuration which originates on the opposite surface of the ($\bar{1}$00) section, before the symmetry determination can be made.

The positive ($\bar{1}$00) configuration resembles the negative ($\bar{1}$00) configuration in appearance, but lies within the alternate pair of quadrants.*

In (0$\bar{1}$0) sections the quadrant positions of the positive and negative configurations are exchanged relative to their quadrant positions in ($\bar{1}$00) sections, but the configurations are otherwise identical with those observed in ($\bar{1}$00) sections.

In (00$\bar{1}$) sections the four paths observed in the negative (00$\bar{1}$) configuration are equally inclined to the c axis, show reflectional symmetry across the (110) and (1$\bar{1}$0) planes, and lie within two diagonally situated quadrants. It follows that the (001) configuration shows twofold symmetry about the c axis. The positive (00$\bar{1}$) configuration is similar to the negative in appearance, but is situated in the alternate pair of quadrants.

In a (100) section (pattern obtained and viewed

from the reverse side of a ($\bar{1}$00) section) the negative configuration is identical with that obtained in ($\bar{1}$00) sections; and the same results are obtained in (010) and (001) sections with respect to (0$\bar{1}$0) and (00$\bar{1}$) sections. The significance of this result is more clearly discerned if one views the section from above and considers simultaneously the negative ($\bar{1}$00) configuration originating from the top surface and the negative (100) configuration originating from the bottom surface.* One then observes that whereas the ($\bar{1}$00) configuration lies in one pair of diagonally situated quadrants, the (100) configuration lies within the alternate pair of diagonally situated quadrants. It follows that the paths originating from the bottom surface are not parallel to those originating from the top surface although the two configurations are formed from symmetrically equivalent paths. This behavior demonstrates that the crystal lacks a center of symmetry and shows that the paths are unidirectional, in exact conformity with the equivalent direction scheme for non-centrosymmetrical point groups.

We determine the point-group symmetry of ADP or KDP from the pattern observed in a ($\bar{1}$00) section as follows: We first determine whether or not the configuration is degenerate. It is clear that the gently dipping path (Fig. 1) does not lie in the (110) plane because to be gently dipping and contained within the (110) plane it would be situated, of necessity, close to the c axis. Since the paths do not lie in the (010) or (110) planes or along coordinate axes, the configuration is non-degenerate. We next assign equivalent points to the paths of the pattern. The negative ($\bar{1}$00) configuration (Fig. 1) consists of four paths having positive components along the a axis, whereas the negative (100) configuration consists of four paths having negative components along the a axis. The point groups of the tetragonal system which satisfy this requirement are $\bar{4}$2m, 42 and 4/m (*International Tables for X-ray Crystallography*, 1952). We can reject 4/m because it is centrosymmetrical and 42 because this group would place an equivalent path in each quadrant of Fig. 1 for each configuration. Only the group $\bar{4}$2m, therefore, provides the qualitative features of the observed pattern. The equivalent directions for the negative ($\bar{1}$00) configuration given by point group $\bar{4}$2m are x, y, z; y, x, z; $x, \bar{y}, \bar{z}$; and $y, \bar{x}, \bar{z}$; those for the negative (100) configuration are $\bar{x}, \bar{y}, z$; $\bar{y}, \bar{x}, z$; $\bar{x}, y, \bar{z}$; and $\bar{y}, x, \bar{z}$. The surface projection of the negative ($\bar{1}$00) configuration consists of the directions yz, xz, $\bar{y}\bar{z}$, and $\bar{x}\bar{z}$, which form a centrosymmetrical surface pattern as observed (Fig. 1). Let the angle that the projection path xz makes with the c axis be θ_1 and let θ_2 be the corresponding angle for the projection path yz. The parameters of the breakdown configuration are then given by (tan θ_1, tan θ_2, 1)

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* The paths are directed towards the probe or point electrode for positive and away from the probe for negative configurations. With the probe as origin and the paths considered as vectors, the negative configuration lies within the half-space occupied by the crystal, but the positive configuration lies in the half-space that is not occupied by the crystal. The positive and negative configurations are identical when the components of the paths in the two patterns have identical magnitudes. In general the positive and negative configurations are not identical and are distinct in ADP and KDP.

* Since the individual breakdown patterns are permanent, the negative configurations originating at the top and bottom surfaces may be examined simultaneously at any time. The configurations are not simultaneously formed.

where $x = z \tan \theta_1$ and $y = z \tan \theta_2$. Since the same angles θ_1 and θ_2 are obtained for any set of projection paths in either the $(\bar{1}00)$ or (100) projection pattern, all the paths are symmetrically equivalent and the point-group symmetry of the crystal is uniquely determined as $\bar{4}2m$ for the breakdown process. The parameters obtained in this way for KDP agree with the parameters that were obtained previously by measuring the inclination and azimuthal angles of the paths (Davisson, 1946, 1948a).

From the configurations observed in (001) and $(00\bar{1})$ sections of ADP or KDP the point-group symmetry can be obtained directly as $\bar{4}2m$ by preparing a breakdown path stereogram, as previously described, and comparing it with the standard stereograms of point-group symmetry (*International Tables for X-ray Crystallography*, 1952).

The above methods of determining the point-group symmetry assume a knowledge of the system of symmetry of the crystal and of its orientation. This prior information is not necessary, since the disposition of the equivalent directions in space alone determines the point-group symmetry and the system of symmetry. When, therefore, a crystal slice of unknown orientation and symmetry is studied, a model of the equivalent directions is constructed from the observed configurations. If any of the configurations are not degenerate, the model will uniquely show the point-group symmetry and will also specify the system of symmetry. The model will frequently also show the location of the coordinate axes; thus the orientation of the crystal slice can often be determined. If all the configurations are degenerate, less information is obtained about the point-group symmetry but usually one is able to determine the system of symmetry and to locate the coordinate axes in cubic, tetragonal and orthorhombic crystals and the c axis in hexagonal crystals.

The proof that the individual pattern is the same whatever the orientation of the section was established by noting that the paths formed from various natural and artificial faces of a seed crystal of KDP lined up with the same setting of the cross-hair eye-piece of a microscope. For ADP, path curvature prevented exact measurements, but the behavior was similar.

NaClO₃ and NaBrO₃

The negative configuration in a $(\bar{1}00)$ section of cubic sodium chlorate is shown in Fig. 2, and similar configurations are observed in $(0\bar{1}0)$ and $(00\bar{1})$ sections. The dominant configuration observed in a principal section, such as $(\bar{1}00)$, consists of six paths which are contained within two diagonally situated quadrants (Davisson & Burstein, 1951). Of the three paths in one quadrant one path dips gently and in surface projection appears to be diagonally situated, while the remaining two paths appear to be symmetrically situated with respect to the above mentioned path and are inclined at about 45° to the normal. Measurements show that

the gently dipping path seldom deviates by more than 1° from the diagonal position. The complete $(\bar{1}00)$ configuration shows twofold symmetry about the normal to the section. The negative (100) configuration, originating at the bottom surface of the section, when viewed from above, lies within the alternate pair of quadrants, but is otherwise identical with the negative $(\bar{1}00)$ configuration. Since the paths from the $(\bar{1}00)$ and the (100) configurations are not parallel, the crystal
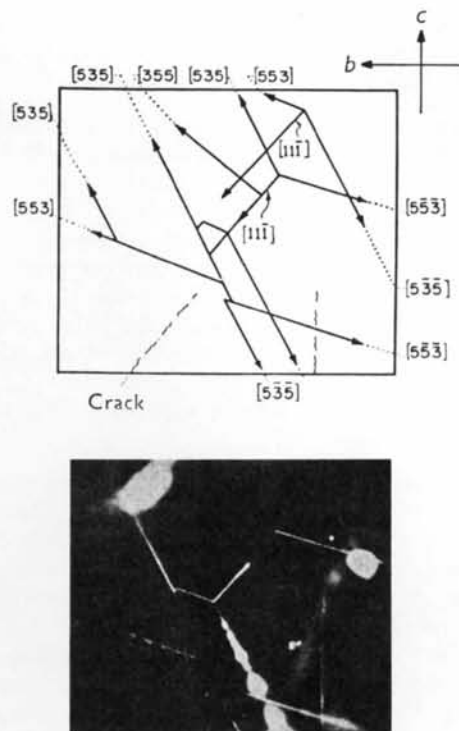

Fig. 2. Electrical breakdown path configurations in a $(\bar{1}00)$ section of NaClO₃. Two degenerate configurations of the pattern are observed with parameters $\langle 553 \rangle$ and $\langle \bar{1}11 \rangle$. The pattern is compatible with threefold symmetry about the body diagonals combined with either twofold rotations or fourfold inversions about the coordinate axes. The point groups 23 and $\bar{4}3m$ can form this pattern.

lacks a center of symmetry. This configuration does not change with temperature, but a different configuration with parameters $[\bar{1}11]$ becomes dominant at low temperature. The $[\bar{1}11]$ configuration is also observed at room temperature, Fig. 2.

The decision as to whether or not the pattern is degenerate depends upon whether the gently dipping path of the configuration observed in the principal sections is diagonally situated or not. If this path is diagonally situated, all the paths of the configuration are contained within the {110} planes and the configuration is degenerate because the {110} planes can show reflectional symmetry in the cubic system. The decision is made after first examining the breakdown pattern in the analogous crystal, sodium bromate. The dominant configuration in NaBrO₃ has the same struc-

ture as that in $NaClO_3$, but is temperature dependent. It is readily verified by examining the shift of the configuration with temperature that the paths in $NaBrO_3$ lie within the {110} planes, and by inference it is concluded that the configuration in $NaClO_3$ is also contained within the {110} planes. It follows that the pattern is degenerate.

The pattern is generated in more than one way, namely by combining either twofold rotations or fourfold inversions about the coordinate axes, with threefold rotations about the body diagonals. We can deduce from the breakdown pattern that $NaClO_3$ and $NaBrO_3$ have the following symmetry properties:

(1) The crystals are cubic, since they exhibit four threefold axes of rotational symmetry.
(2) They lack a center of symmetry.
(3) The coordinate axes do not show fourfold rotational symmetry, but it is not determined whether they show fourfold inversion symmetry or twofold rotational symmetry.
(4) The diagonal $\langle 110 \rangle$ axes do not show rotational symmetry, since these rotations would send the paths into the unoccupied quadrants.
(5) The {100} planes are not reflecting for the same reason as (4).

The reflectional symmetry of the {110} planes is undetermined, since the paths lie in these planes. The pattern thus conforms with the point group 23 and with the point group $\overline{4}3m$ in which the reflectional symmetry is inoperative owing to the degenerate configurations. The fact that the paths in $NaClO_3$ and $NaBrO_3$ are constrained to lie within the {110} planes provides no basis for believing that these planes are reflecting. It is important to note that the breakdown pattern does not predict a symmetry that is higher than the accepted symmetry of the crystal, which is point group 23,* since in cases of degeneracy the breakdown pattern provides no basis for distinguishing between the unresolved point groups.

The alkali halide crystals

The star pattern observed in the lithium halides (Davisson, 1948a) and in KF and NaCl (Davisson, 1948b, 1953, 1954) has the same symmetry as the dominant configuration of $NaClO_3$, except that the set of three paths appears in every octant of the crystal. Since the paths lie in the {110} planes the configuration is degenerate. The pattern can be generated in two ways, namely by combining threefold rotations about the body diagonals either with fourfold rotations about the coordinate axes or with reflections across the principal planes. The point groups $2/m\overline{3}$, $4/m\overline{3}2/m$, and 432 are compatible with the degenerate pattern; the point groups 23 and $\overline{4}3m$ are incompatible. It is important to note that although this configuration is

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* The space group obtained by X-rays is $P2_13$ which requires 23 as the isomorphous point group.

centrosymmetrical, the crystal is not necessarily centrosymmetrical, since the pattern can be generated by the point group 432.

Orthorhombic sulphur

The dominant breakdown configuration in orthorhombic sulphur grown from a CS_2 solution is degenerate, since it consists of the paths [100], [0yz] and [0$\bar{y}z$], which lie within the principal planes (Davisson, 1946, 1948a). Since the configuration is centrosymmetrical, we can reject the point group mm2, but we are not able to distinguish between 222 and $2/m2/m2/m$. In an effort to obtain a non-degenerate pattern, we have produced configurations at low temperature ($-195°$ C.) in (111) sections and have observed a few instances (in all, three observations) where one of the [0yz] paths formed a fork which seemed to show reflectional symmetry across the (100) plane.* On the basis of this evidence we infer that the symmetry of orthorhombic sulphur is probably $2/m2/m2/m$ for the breakdown process, in agreement with the accepted symmetry (Warren & Burwell, 1935).

Apatite

The (0001) configuration of apatite shows paths in sixfold general positions. The (000$\bar{1}$) configuration is not shifted with respect to the (0001) configuration and is thus its mirror image. Since the pattern is non-degenerate, the symmetry of apatite for the breakdown process is $6/m$. The point group $6/m$ for apatite is also obtained from morphological (Groth, 1908, p. 826) and X-ray diffraction studies (Náray-Szabó, 1930).

Monoclinic and triclinic crystals

In contrast with the breakdown configurations in crystals of higher symmetry, which are usually degenerate, the configurations in all triclinic and in most monoclinic crystals will be non-degenerate. Triclinic crystals will never show degenerate configurations because they contain no planes or axes of symmetry. For monoclinic crystals there are three point groups to consider, namely 2, m and $2/m$. If the crystal slice is cut parallel to the symmetry plane, the volume paths will not lie in the symmetry plane and a degenerate configuration will be obtained only when the paths lie parallel to the symmetry axis. Since most crystals will show more than one breakdown configuration, it follows that we can expect most monoclinic crystals to show a non-degenerate breakdown pattern.

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* Observational evidence using a stereoscope microscope. The geometry of the fork was established by noting that the [100] breakdown paths lay parallel to the fork plane. No instances of path forking were observed in principal sections.

Colemanite, $2CaO.3B_2O_3.5H_2O$

The breakdown configurations in colemanite show the symmetry $2/m$ uniquely at 150° C. and at 30° C. Each configuration consists of a set of four paths showing twofold symmetry about the [010] axis and reflection across the (010) plane. While several configurations are usually formed during breakdown they have only slightly different orientations. The result is that many of the paths have a curved or segmented aspect, since they transform from one configuration to the next as they proceed through the crystal. The existence of multiple configurations of the above type is characteristic of crystals that show a temperature dependence of breakdown path orientation, such as the star patterns in the alkali halides (Davisson, 1946, 1948a). In colemanite we find that the dominant configuration shifts with temperature as follows: Viewed in a (010) slice, it lies in a $(x0z)$ plane which deviates from a datum $(x0z)$ plane, that is given by the extinction position of the slice, by 12° at 150° C., by 5° at 30° C., and by 1° at -195° C.

At first glance the configuration at -195° C. seems to show the symmetry $2/m$, but it is noted that all four paths which comprise the configuration do not seem to be equally abundant. A detailed study of this effect is in progress.

While the breakdown studies, in agreement with X-ray studies (Christ, 1953), seem to indicate that colemanite is centrosymmetrical, we have found by other tests that the crystal lacks a center.* Our present view is that the structure of colemanite consists of a symmetrical oxygen framework, showing the symmetry $2/m$, but that some other constituents, presumably the hydrogen or boron atoms, are in non-

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* We have found colemanite to be both pyroelectric and piezoelectric. The facts (1) that colemanite develops equal and opposite charge on opposing (010) faces when the temperature is changed uniformly and (2) that the polarity of the charge developed upon a given (010) face is independent of the direction of an applied thermal gradient, indicate that the effect is due either to vectorial pyroelectricity or to piezoelectricity and not to tensorial (quadropole) pyroelectricity, electrification, or to a thermoelectric effect. The pyroelectric constant of colemanite shows an exceedingly high and narrow peak at -2·5° C. (300 statcoulombs cm.$^{-2}$ deg.$^{-1}$, peak value; 3° C. wide at half-peak value—measurements calibrated against a tourmaline standard). The peak has a tail which extends to low temperatures, but on the high-temperature side the constant is low at 30° C. (from 1 to 0·1 in the above units) and it vanishes below 100° C. The details of this and other properties of colemanite will be presented in detail at a later date.

central positions, showing the symmetry 2. The existence of a symmetrical breakdown pattern suggests that the influence of the hydrogen or boron atoms upon the scattering of electrons may be insignificant in comparison with the scattering from the oxygen atoms.

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