equatorial plane at the central spot. In this case the method is further limited to class I crystals. For such preliminary adjustments either Laue or symmetrical oscillation photographs can be used.
(c) Lonsdale (1947) has suggested the use of a flat film perpendicular to the rotation axis for determining small arc corrections from a Laue photograph when a symmetry axis is being adjusted parallel to the rotation axis. The same method of calculation can be used, taking reflexions related by a diad axis of symmetry instead of by a plane. The main difficulties lie in deter-
mining the point where the rotation axis cuts the film, and the crystal-film distance. A trial-and-error process may have to be resorted to, using estimated instead of calculated adjustments.

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# Crystal Symmetry and Physical Properties: Application of Group Theory 

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#### Abstract

The paper gives a brief account of group-theoretical methods of studying the effect of symmetry on all possible physical properties (known and already measured or not known) which depend on crystal symmetry; based on the fact that all such properties represent the relation between two quantities each of which may be a scalar, a vector, or a tensor. Tables are given showing the character of the transformation matrices for each possible combination of the above quantities, the number of independent constants needed to describe the corresponding phenomenon in each of the 32 classes, and actual examples (where known) of physical properties corresponding to the different possible combinations. The 32 crystal classes are reduced to 11 in all cases where centro-symmetrical properties are dealt with. When comparison is made with results of other methods of considering the same problems, discrepancies are found in the case of the photo-elastic coefficients and the thirdorder elastic coefficients.

All the properties considered above are such as will remain invariant under a transformation of axes according to any symmetry operation. There are other properties, such as enantiomorphism and optical activity, which change sign for an operation of rotation reflexion. The numbers of independent constants in each of the 32 classes are deduced for these properties also.


## 1. Introduction

Physical properties of substances generally express the relation between two quantities. These may be scalars, vectors, second- or higher-order tensors, all differing from one another by their transformation properties. Voigt made the transformation properties of the quantities involved in a physical relation the basis for the classification of crystal properties, thus distinguishing scalar-scalar relations (density), scalar-vector relations (pyro-electricity), vector-vector relations (dielectric polarization), tensor-tensor relations (elasticity), and so on. Each of these relations requires a number of independent coefficients connecting the components of the quantities involved, and, without assuming any symmetry of the crystal, the number of independent coefficients in the case of linear relations is the product of the numbers of independent components of the quantities being related. In crystals with symmetry elements, this maximum number of coefficients will be reduced. In order to find the reduction, produced by a symmetry element, Voigt transforms the
axes of reference according to the symmetry element and demands that this transformation have no influence on the values of the coefficients expressing the relation of the physical quantities. It follows by this direct method of transformation that a number of coefficients must be zero, while others are equal. The systems of non-vanishing as well as of independent constants for various properties were thus derived in considerable detail by Voigt (1910) and by Pockels (1906). Love (1928), Wooster (1938), Cady (1946), Mason (1947) and others have subsequently dealt with the subject.

The fact that the symmetry operations of a crystal form a group allows the application of group theory to the study of the effect of symmetry on the physical properties of crystals. This very powerful method can be used as a valuable check on the direct process of deriving the non-vanishing constants in each of the 32 crystal classes. Thus Jahn (1937) made use of group theory for deducing the number of independent parameters and the non-vanishing elastic constants of
crystals. One of us (Bhagavantam, 1942) gave a somewhat different method by which group theory can be used for deriving the numbers of independent constants in the 32 crystal classes for any property. This method was applied to the cases of optical, elastic and photoelastic properties. Discrepancies were found in respect of photo-elasticity for certain crystal classes between the results thus obtained and those given earlier by Pockels. The method has since been extended to other physical properties in subsequent papers (Saksena, 1944; Suryanarayana, 1945, 1946; Bhagavantam \& Suryanarayana, 1947). It is now proposed to give a connected account and to apply it in a general manner to all the possible physical properties, already measured or otherwise, which depend on crystallographic symmetry.

## 2. Description of the method

Consider the transformation properties under any symmetry operation of a scalar, a vector, a second-order symmetric tensor and a second-order unsymmetric tensor. A scalar remains unchanged, the components of a vector transform as the Cartesian co-ordinates, the components of a symmetric tensor as the products of Cartesian co-ordinates with some additional conditions, the components of an unsymmetric tensor as simple products of Cartesian co-ordinates. Thus, under an operation $R_{\phi}$ consisting of a rotation about the $z$ axis through $\phi$ or a rotation reflexion through $\phi$, the components of a vector, a symmetric tensor and an unsymmetric tensor transform according to the equations (1), (2) and (3) respectively. The upper and lower sign, where an alternative occurs, refer respectively to a pure rotation and a rotation reflexion.

$$
\begin{align*}
& p_{x} \rightarrow p_{x} \cos \phi+p_{y} \sin \phi, \\
& \left.p_{y} \rightarrow-p_{x} \sin \phi+p_{y} \cos \phi, \quad p_{z} \rightarrow \pm p_{z} ;\right\}  \tag{1}\\
& \dot{\alpha}_{x x} \rightarrow \alpha_{x x} \cos ^{2} \phi+\alpha_{y y} \sin ^{2} \phi+2 \alpha_{x y} \sin \phi \cos \phi, \\
& \alpha_{y y} \rightarrow \alpha_{x x} \sin ^{2} \phi+\alpha_{y y} \cos ^{2} \phi-2 \alpha_{x y} \sin \phi \cos \phi, \\
& \alpha_{z z} \rightarrow \alpha_{z z}, \\
& \alpha_{y z} \rightarrow \pm \alpha_{y z} \cos \phi \mp \alpha_{z x} \sin \phi, \\
& \alpha_{z x} \rightarrow \pm \alpha_{y z} \sin \phi \pm \alpha_{z x} \cos \phi, \\
& \alpha_{x y} \rightarrow-\alpha_{x x} \sin \phi \cos \phi+\alpha_{y y} \sin \phi \cos \phi \\
& +\alpha_{x y}\left(\cos ^{2} \phi-\sin ^{2} \phi\right) ; \\
& \beta_{x x} \rightarrow \beta_{x x} \cos ^{2} \phi+\beta_{y y} \sin ^{2} \phi+\left(\beta_{x y}+\beta_{y x}\right) \sin \phi \cos \phi, 7  \tag{4}\\
& \beta_{y y} \rightarrow \beta_{x x} \sin ^{2} \phi+\beta_{y y} \cos ^{2} \phi-\left(\beta_{x y}+\beta_{y x}\right) \sin \phi \cos \phi, \\
& \beta_{z z} \rightarrow \beta_{z z}, \\
& \beta_{y z} \rightarrow \mp \beta_{x z} \sin \phi \pm \beta_{y z} \cos \phi, \\
& \beta_{z y} \rightarrow \mp \beta_{z x} \sin \phi \pm \beta_{z y} \cos \phi, \\
& \beta_{z x} \rightarrow \pm \beta_{z x} \cos \phi \pm \beta_{z y} \sin \phi, \\
& \beta_{x z} \rightarrow \pm \beta_{x z} \cos \phi \pm \beta_{y z} \sin \phi, \\
& \beta_{x y} \rightarrow-\beta_{x x} \sin \phi \cos \phi+\beta_{y y} \sin \phi \cos \phi \\
& +\beta_{x y} \cos ^{2} \phi-\beta_{y x} \sin ^{2} \phi, \\
& \beta_{y x} \rightarrow-\beta_{x x} \sin \phi \cos \phi+\beta_{y y} \sin \phi \cos \phi \\
& -\beta_{x y} \sin ^{2} \phi+\beta_{y x} \cos ^{2} \phi .
\end{align*}
$$

$$
1
$$

These transformations may be regarded as linear substitutions. The characters of the three transformation matrices are easily seen to be respectively

$$
(2 \cos \phi \pm 1), \quad\left(4 \cos ^{2} \phi \pm 2 \cos \phi\right)
$$

and $\quad\left(4 \cos ^{2} \phi \pm 4 \cos \phi+1\right)$.
Similarly, the transformation matrix and the respective character for a tensor of a higher order representing any given physical property can be deduced. It will be noted that the character for an unsymmetric tensor having nine components is the square of the character for the vector of three components. Similarly, the character for a third-order tensor (piezo-electric constants giving the relation between a vector and a symmetric tensor) is the product of the characters appropriate to a vector and a symmetric tensor, and so on. When special relations exist between the various components, the character has, however, to be deduced by writing down the full transformation matrix itself. For example, the elastic coefficients show how a stress tensor (second-order symmetric) gives rise to a strain tensor (second-order symmetric), but the maximum number of such coefficients is only 21 , and not 36, because of the special relations* $c_{i k}=c_{k i}$, and the character in such a case has to be evaluated independently. Similar considerations apply to the higherorder elastic coefficients which reduce to 56 from being 126. These characters are given in column 3 of Table 1.

Considering, for example, the above symmetric tensor of six components, the linear substitutions (2) constitute a reducible representation of the group $G$ of symmetry operations of any crystal class. Six mutually orthogonal and independent linear combinations of the above components may be found in such a way that they fall into six or less number of sets, the members in each set transforming among themselves by every operation of the group $G$. These will constitute the basis for a new and completely reducible representation of the group $G$. The character appropriate to any element $R$ in this representation will be the same as that obtained before, since the two are equivalent. It is now easy to find $n_{i}$, the number of times a particular irreducible representation repeats itself, in the representation consisting of the new variables with the help of the general formula

$$
n_{i}=\frac{1}{N} \sum_{j} h_{j} \chi_{j}^{\prime}(R) \chi_{i}(R)
$$

$N$ is the total number of elements of the group $G$, and $h_{j}$ is the number of elements in the $j$ th class. $\chi_{j}^{\prime}(R)$ is the character of the appropriate transformation matrix relative to the operation $R$, as given in Table 1, and $\chi_{i}(R)$ is the character relative to the operation $R$ in the particular irreducible representation. $\dagger$

By the application of Voigt's condition, we demand that in the case of any specified physical property

[^0]
represented by such a tensor (row $3 a$ of Table 1) only those combinations of parameters in respect of any particular crystal can survive which have the entire symmetry of the crystal. Thus we want to know the number of combinations that remain invariant for all operations $R$ of the crystallographic group $G$. This means that we need only find the value of $n_{i}$ appropriate to the total symmetric irreducible representation. This is characterized by the fact that $\chi_{i}(R)=1$ for all $R$. In this case $\chi_{j}^{\prime}(R)$ has already been shown to be equal to ( $4 \cos ^{2} \phi \pm 2 \cos \phi$ ).

Similar arguments hold for the various coefficients describing other phenomena. In each case, the number $n_{i}$ represents the number of independent constants needed to describe the phenomenon in the particular crystal class.

## 3. Results

Table 1 gives the physical properties arranged systematically in order of increasing complexity and is selfexplanatory. Rows 1 to 10 refer to first-order phenomena, whereas rows 11, 12 and 13 are representative of higher-order phenomena. The list of physical properties in any row is only representative and is not claimed to be complete. Where no representative physical property is known to exist, a line is drawn.

In Table 2 are given the 32 crystal classes or point groups with their well-known symbols. Symbols representing the symmetry elements under each crystal class have the usual significance. The numbers of independent constants for each of the properties of Table 1 needed by the 32 classes, as derived from formula (4), are given in Table 2. The elements of symmetry given in column 5 for each of the point groups are divided into conjugate classes of the group. In the sub-columns headed by 8 and 12 are given the photo-elastic coefficients and the third-order elastic coefficients, in which discrepancies were noticed and pointed out first by the application of this method. The division of the 32 crystal classes into 11 Obergruppen in all cases when we are dealing with centro-symmetrical properties is especially evident in sub-columns headed by 8 . and higher numbers in Table 2. Each of these Obergruppen consists of a class with centre of inversion as one of the symmetry operations, and of all its immediate subgroups.

## 4. Enantiomorphism and optical activity

For the properties dealt with above we have to find the value of $n_{i}$ appropriate to the total symmetric irreducible representation because we want to know the number of combinations that remain invariant for all operations $R$ of the crystallographic group G. In addition, there are other properties for which we have to find the number of combinations that remain invariant for operations of pure rotations, and change sign for operations of rotation reflexions. Enantiomorphism and optical activity are wellil-known examples of such phenomena.

Enantiomorphism is the existence of forms which are mirror images of each other. This is obviously represented by a single constant. Optical activity is represented by a second-order symmetric tensor which is the gyration tensor with six components. The sign of rotation of the plane of polarization remains invariant under an operation of pure rotation and changes sign for a rotation reflexion. In order, therefore, to find the number of independent constants required to specify the gyration tensor, we should find the number of independent and orthogonal linear combinations of the components which will transform so as to remain invariant if the symmetry operation is a pure rotation and change sign if the symmetry operation is a rotation reflexion. Hence the appropriate irreducible representation for which the number of combinations has to be found is not the total symmetric one but the antisymmetric irreducible representation with character $\chi_{i}= \pm 1$, the upper sign referring to pure rotations and the lower referring to rotation reflexions. The character $\chi_{j}^{\prime}$ of the transformation matrix for the gyration tensor is again ( $4 \cos ^{2} \phi \pm 2 \cos \phi$ ), and for enantiomorphism it is unity. Using the general formula (4) with the new character, the numbers of constants for the 32 classes are easily obtained. They are given in the sub-columns headed by En. and Op. A. in Table 2. They all agree with the known numbers.

This principle can be extended to the other characters $\chi_{j}^{\prime}$ contained in Table 1. Voigt has considered the cases of what he calls a pseudo-scalar, axial vector and axial tensor, and physical properties represented by these and the combination of these with the usual polar vector and polar tensor. He has deduced the schemes of non-vanishing constants for these properties irrespective of whether these properties have a real existence or not. The numbers in all these cases agree with those that would be obtained by combining the value of $\pm 1$ for $\chi_{i}(R)$ with the $\chi_{j}^{\prime}(R)$ in the first six rows of Table 1, namely, $1,(2 \cos \phi \pm 1),\left(4 \cos ^{2} \phi \pm 2 \cos \phi\right)$, $\left(4 \cos ^{2} \phi \pm 4 \cos \phi+1\right)$ and ( $\left.8 \cos ^{3} \phi \pm 8 \cos ^{2} \phi+2 \cos \phi\right)$. Numbers in these cases, except for enantiomorphism and optical activity, are not given in Table 2 as they are not all represented by known physical properties. Voigt claims that the second and the last of the above are represented by pyro-magnetism and piezo-niagnetism respectively. An extension of this principle to some of the more complicated tensors in Table 1 is easy, but it is doubtful whether the results represent any possible physical phenomena.

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# Photo-elastic Behaviour of Ammonium Alum Crystals 

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To test an earlier prediction by Bhagavantam, based on a group theoretical method, that the $T-23$ and $T_{n}-2 / m \overline{3}$ classes of the cubic system need four independent constants, instead of three, for describing their photo-elastic properties, crystals of ammonium alum belonging to the $T_{h}-2 / m \overline{3}$ class were studied completely. It was found that the crystal needs four independent constants and all the four stress-optical constants of alum have been determined. For sodium $D$ light, they are

$$
\begin{aligned}
\left(q_{11}-q_{12}\right) & =-5.93 \times 10^{-13}, & \left(q_{11}-q_{13}\right) & =-5.25 \times 10^{-13}, \\
q_{11} & =5.5 \times 10_{44}=-1.15 \times 10^{-13}, & q_{12} & =11.6 \times 10^{-13},
\end{aligned} \begin{array}{ll}
q_{13} & =10.9 \times 10^{-13} \mathrm{~cm} .^{2} \mathrm{dyne}^{-1} .
\end{array}
$$

The values of the strain-optical constants are

$$
\begin{aligned}
& \left(p_{11}-p_{12}\right)=-0.0854, \quad\left(p_{11}-p_{13}\right)=-0.0756, \quad p_{44}=-0.0092, \\
& p_{11}=0.38, \quad \quad p_{12}=0.46, \quad p_{13}=0.45 \text {. }
\end{aligned}
$$

## 1. Introduction

In the preceding paper in this journal (Bhagavantam \& Suryanarayana, 1949) a group theoretical method is given of deriving the number of independent constants needed to describe any physical property in the 32 crystal classes. The numbers found in the case of photo-elasticity are at variance with those given by Pockels (1889, 1906, p. 460) and current in the literature for the classes

$$
\begin{aligned}
& C_{4}-4, S_{4}-\overline{4}, C_{4 h}-4 / m ; C_{3}-3, S_{6}-\overline{3}, C_{3 h}-3 / m \\
& C_{6}-6, C_{6 h}-6 / m ; T-23 \text { and } T_{h}-2 / m \overline{3}
\end{aligned}
$$

The non-vanishing stress-optical coefficients, when worked out directly for all the 32 classes, confirm the findings of the group-theoretical method. They show that in the case of photo-elasticity the 32 crystal classes are divided into eleven Obergruppen, and not nine as was formerly believed to be the case.

The present experimental investigation of the photoelastic behaviour of certain crystals is undertaken to clear the existing discrepancy. While, according to Pockels, the cubic classes require only three constants, the new theory predicts four independent photo-elastic constants for the class $T_{h}-2 / m \overline{3}$. Of the cubic crystals with which Pockels himself had worked, two, namely
potassium alum and ammonium alum, belong to this class (Wyckoff, 1931). The original paper of Pockels (1889) dealing with the alums shows that the orientations of his prisms were not suitable for deciding the present issue. We therefore made further measurements on alums, of which those on potassium alum have already been published (Bhagavantam \& Suryanarayana, 1947). Results on ammonium alum crystals now obtained are reported here. They are in entire agreement with the findings of the group-theoretical method.

## 2. Theoretical considerations

The photo-elastic behaviour of the $T-23$ and $T_{h}-2 / m \overline{3}$ classes of crystals is given by the equations

$$
\left.\begin{array}{l}
B_{11}-B=-\left(q_{11} P_{x x}+q_{12} P_{y y}+q_{13} P_{z z}\right), B_{23}=-q_{44} P_{y z}, \\
B_{22}-B=-\left(q_{13} P_{x x}+q_{11} P_{y y}+q_{12} P_{z z}\right), B_{31}=-q_{44} P_{z x}, \\
B_{33}-B=-\left(q_{12} P_{x x}+q_{13} P_{y y}+q_{11} P_{z z}\right), B_{12}=-q_{44} P_{x y} . \tag{1}
\end{array}\right\}
$$

In these equations $B=1 / n^{2}, B_{11}^{2}=1 / n_{11}^{2}$, etc., where $n$ is the refractive index of the undeformed cubic crystal, $n_{11}$ etc., are the components describing the Fresnel ellipsoid in the deformed condition, $P_{x x} \ldots P_{x y}$ are the components of stress, and $q_{11}, q_{12}, q_{13}$ and $q_{44}$ are the


[^0]:    * Voigt's notation is used: $i$ and $k$ run from 1 to 6.
    $\dagger$ For a derivation of this formula and a fuller explanation of the symbols, reference may be made to Bhagavantam and Venkatarayudu (1948).

