Irregular Ferroelectrics

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The ferroelectrics are divided into the regular and the irregular ferroelectrics. The regular ferroelectrics crystallographically must belong to the polar groups. The irregular ferroelectrics are divided into those belonging to the polar groups and those belonging to the noncentrosymmetrical groups except the polar groups. The latter irregular ferroelectrics are scarcely expected to exist. All of the hitherto discovered irregular ferroelectrics belong to the former. This paper deals with the former irregular ferroelectrics exclusively and refers to them as simply the "irregular ferroelectrics. "In the Grst place the classification of the irregular ferroelectrics is attempted. It is found that the irregular ferroelectrics are divisible into 11kinds in accordance with their point groups, Bravais lattices, and types of state transition. A new symbol is given to each of these kinds. Secondly, it is systematically shown how the tensorial properties of each kind of irregular ferroelectrics should be changed with the state transition. The kinds of tensors considered are the polar and axial tensors of ranks two, three, and four. This study is aimed to serve not only for predicting the manners of change of the tensorial properties in the irregular ferroelectrics, but also for identifying the kind of an irregular ferroelectric and for judging regularity or irregularity of a ferroelectric. Lastly, the gyroelectricity and hypergyroelectricity in the irregular ferroelectrics are examined. Those crystals have been referred to as being gyroelectric and hypergyroelectric whose gyration and electrogyration, respectively, are nonzero and reversed in sign by means of a suitable biasing electric 6eld. (Electrogyration means the rate of change of the gyration with the biasing electric Geld at zero value of the biasing electric Geld.) It is found that, of the 11 kinds of irregular ferroelectrics, ² kinds are gyroelectric, 7 hypergyroelectric, and the remaining 2 neither gyroelectric nor hypergyroelectric.

I. INTRODUCTION

 \mathbf{W}^{E} have adopted as a most reasonable definition of ferroelectricity the following one': When a crystal plate, with certain Miller indices, of a crystal has two stable states (diferent in polarization) at no electric field and can alternate between these states by means of a suitable alternating electric held, then the crystal plate or the crystal is said to be ferroelectric; here the two stable states are assumed to be identical or enantiomorphous in crystal structure and to be equal in plate thickness. In this definition of ferroelectricity the equality in plate thickness of the two stable states is not to be overlooked. We refer to the direction of the normal to a ferroelectric crystal-plate as a "ferroelectric direction" of its parent crystal.

We have introduced the concept of the regular ferroelectrics': A ferroelectric crystal is said to be regular when (i) in any crystal plate with any Miller indices of the crystal the space lattice in one of the two stable states is parallel to the space lattice in the other, and (ii) the notion of the two stable states is possible not only for the individual crystal-plates but for the crystal as a whole. Since all the regular ferroelectrics crystallographically belong to the polar groups' and since, on the other hand, the ferroelectrics belonging to the polar groups satisfy the second condition if they only satisfy the first condition, it can also be stated that the regular ferroelectrics are those ferroelectrics which belong to the polar groups and satisfy the first condition for regularity, i.e., the condition of lattice parallelism. All ferroelectrics are divided into the regular ferroelectrics and the ferroelectrics which are not regular, namely, the *irregular* ferroelectrics.²

The irregular ferroelectrics are divided into those belonging to the polar groups and those belonging to the nonpolar, but noncentrosymmetrical, groups. It has been reasoned' that the latter irregular ferroelectrics are scarcely expected to exist; in fact no such ferroelectric has yet been discovered. As examples of the former irregular ferroelectrics there are Rochelle salt and KDP (potassium dihydrogen phosphate). In the present paper we deal with the former irregular ferroelectrics exclusively, and henceforth refer to them as simply the "irregular ferroelectrics."

In the regular ferroelectrics most directions are ferroelectric (any direction not nearly perpendicular to the direction of the spontaneous polarization vector³

¹ K. Aizu, Rev. Mod. Phys. 34, 550 (1962).

² We distinguish "the two stable states of the *crystal*" from "the two stable states of the *crystal plate.*" It may be evident that the former notion cannot be conceived for the ferroelectrics not subject to the first condition. Hence the former notion is possible only for the regular ferroelectrics. For the irregular ferroelectrics we can only have the latter notion concerning individual crystalplates; in this case it does not matter whether, or not, one imagine for each of the two stable states of the crystal plate an *infinit* crystal by unlimitedly continuing the crystal plate in its normal direction. (For details see Ref. 1.)

The author considers that the (ferroelectric) spontaneous polarization or the spontaneous polarization vector is not to be a priori introduced into the definition of ferroelectricity, but is to be a posteriori defined and proved on its existence. The "spontaneous *a posteriori* defined and proved on its existence. The "spontaneous
vector." For every ferroelectric crystal-plate it is possible to define
and prove a (ferroelectric) spontaneous polarization, which muss
be independent o taneous polarization vector, which must be independent of the reference structure (or the unit cell), the crystal-plate orientation, and the crystal-plate boundaries. (For details see Ref. 1.)

may be ferroelectric), while in the irregular ferroelectrics it is considered that there is only one ferroelectric direction.⁴ In view of symmetry, this unique direction must agree with the direction of the crystallographic unique axis in all polar groups except 1 and m , and be parallel to the mirror plane of symmetry in the polar group m.

In this paper we attempt to treat, concerning the irregular ferroelectrics, the same problems as we have treated, concerning the regular ferroelectrics, in Sec. 6.5 of Ref. 1 and in Refs. 5 and 6. First, in Sec. 2, the irregular ferroelectrics are classified into kinds in accordance with their point groups, Bravais lattices, and types of state transition. This corresponds to the classification of the regular ferroelectrics into 19 kinds.¹ In Ref. 5 all regular kinds have been given new symbols:

r1, rm, r2, rmm2, r4-I, r4-II, r4mm, r6-I, r6-II, r6mm, r3R-I, r3E-II, r3mR, r3P-I, r3P-II, r3P-III, v3P-IV, r3mP-I, r3mP-II.

It is also convenient to give new symbols to all irregular kinds.

When the irregular ferroelectric crystal-plates undergo the state transition, their tensorial properties are changed in a manner unique and definite to each of their kinds. In Sec. 3 a systematic investigation is made into these manners of change. The kinds of tensors examined are the polar and axial tensors of ranks two, three, and four. The second-rank tensors need not be symmetric, while the third- and fourth-rank tensors are assumed to be partially symmetric. The results of this section are expected to serve not only for predicting the manners of change of the tensorial properties in the irregular ferroelectric crystal-plates, but also for identifying the kind of an irregular ferroelectric crystal, for determining the rotation axes in the irregular ferroelectrics of rotation type (see Secs. 2 and 3), and for judging regularity or irregularity of a ferroelectric crystal. This section corresponds to Sec. 3 of Ref. 5.

In Ref. 6, we referred to a crystal as being gyroelectric (or as a gyroelectric) if its optical rotatory power or gyration is nonzero at no biasing electric field and reversible in sign by means of a suitable biasing electric field. We referred to a crystal as being $hyper$ gyroelectric (or as a hypergyroelectric) if its electrogyration is nonzero and reversible in sign by means of a suitable biasing electric field. Here electrogyration means the rate of change of the gyration with the biasing electric 6eld at zero value of the biasing electric field. (The rate of change of the gyration with the stress at zero value of the stress will be referred to as "piezogyration. ") It is evident from the definitions that the gyroelectric and the hypergyroelectric crystals must be ferroelectric. We have especially referred' to a gyroelectric and a hypergyroelectric which is regularly ferroelectric as a regular gyroelectric and a regular hypergyroelectric, respectively. It has been shown' that, of the 19 kinds of regular ferroelectrics, 9 kinds are gyroelectric, 5 hypergyroelectric, and the remaining 5 neither gyroelectric nor hypergyroelectric.

We shall refer to a gyroelectric and a hypergyroelectric which is *irregularly* ferroelectric as an *irregular* gyroelectric and an irregular hypergyroelectric, respectively. In Sec. 4 of the present paper a determination is made as to which of the irregular ferroelectric crystalplates should be gyroelectric and which hypergyroelectric; there, the study in Sec. 3 will help.

2. CLASSIFICATION OF THE IRREGULAR FERROELECTRICS

We consider only the crystal plates perpendicular to the ferroelectric direction. A set of rectangular coordinate axes x , y , z is taken with the z axis parallel to the ferroelectric direction; these axes are spatially fixed and independent of the state transition. Since the two stable states S and S^* are either identical or enantiomorphous in crystal structure, one of them should be obtained by performing upon the other a certain operation F belonging to the rotation group. F can be represented by an orthogonal matrix

such that an arbitrary point (x,y,z) is changed by **F** to the point (x', y', z') :

$$
\begin{bmatrix} x' \\ y' \\ z' \end{bmatrix} = \begin{bmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix}.
$$

The condition for orthogonality is

or

$$
\begin{bmatrix} a_{11} & a_{12} & a_{13} \ a_{21} & a_{22} & a_{23} \ a_{31} & a_{32} & a_{33} \end{bmatrix} \begin{bmatrix} a_{11} & a_{21} & a_{31} \ a_{12} & a_{22} & a_{32} \ a_{13} & a_{23} & a_{33} \end{bmatrix} = \begin{bmatrix} 1 & 0 & 0 \ 0 & 1 & 0 \ 0 & 0 & 1 \end{bmatrix}.
$$
\n(2.1)

Suppose that two arbitrary points (x_1, y_1, z_1) and (x_2,y_2,z_2) are changed by **F** to the points (x_1',y_1',z_1') and (x_2', y_2', z_2') , respectively. Then, since **F** must not alter the thickness of the crystal plate, F must be such that either

$$
z_1 - z_2 = z_1' - z_2', \qquad (2.2)
$$

$$
z_1 - z_2 = -(z_1' - z_2'). \qquad (2.3)
$$

Considering, however, that S and S^* are the ferroelectric two states, \bf{F} must satisfy (2.3).

⁴ This statement does not deny that even for other directions than the only ferroelectric-direction *some sort of* state transition
or polarization reversal may occur. For such directions, the two stable states of the crystal plate should differ in plate thickness, or else a reorientation of the crystallographic axes might arise during the repetition of the state transition so that the normal to the crystal-plate sample might become the ferroelectric direction

of the crystal.
⁵ K. Aizu, Phys. Rev. 133, A1350 (1964).
⁶ K. Aizu, Phys. Rev. 133, A1584 (1964).

From the conditions (2.1) and (2.3) it is derived that F must be equal to either

$$
\mathbf{F}_{-}(\alpha) \equiv \begin{bmatrix} \cos \alpha & -\sin \alpha & 0 \\ \sin \alpha & \cos \alpha & 0 \\ 0 & 0 & -1 \end{bmatrix}
$$
 (2.4)

or

$$
\mathbf{F}_{+}(\beta) \equiv \begin{bmatrix} \cos\beta & \sin\beta & 0\\ \sin\beta & -\cos\beta & 0\\ 0 & 0 & -1 \end{bmatrix} . \tag{2.5}
$$

The parameters α and β can be limited within the ranges

$$
-\pi < \alpha \leq \pi, \quad -\pi < \beta \leq \pi, \tag{2.6}
$$

respectively. It is evident that

$$
\det \mathbf{F}_{-}(\alpha) = -1, \quad \det \mathbf{F}_{+}(\beta) = +1. \tag{2.7}
$$

("det" is an abbreviation of "determinant. ") $\mathbf{F}_{\text{m}}(\alpha)$ can be rewritten as

$$
\mathbf{F}_{-}(\alpha) = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{bmatrix} \begin{bmatrix} \cos \alpha & -\sin \alpha & 0 \\ \sin \alpha & \cos \alpha & 0 \\ 0 & 0 & 1 \end{bmatrix} . (2.8)
$$

The matrix

$$
\begin{bmatrix}\n\cos\alpha & -\sin\alpha & 0 \\
\sin\alpha & \cos\alpha & 0 \\
0 & 0 & 1\n\end{bmatrix}
$$
\n(2.9)

represents the rotation operation about the z axis by an angle of α . The matrix

$$
\begin{bmatrix} 1 & 0 & 1 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{bmatrix} \tag{2.10}
$$

represents the reflection operation across the xy plane. $F_{-\alpha}$ can, therefore, be interpreted as an α rotation about the z axis followed by a reflection across the xy plane. In fact, the order of these two operations is immaterial, for the matrices (2.9) and (2.10) are commutable. It may be obvious that $\mathbf{F}_{+}(\beta)$ represents the π rotation about the axis which lies on the xy plane and makes an angle of $\frac{1}{2}\beta$ with the x axis. The relationship in sense between the angle α or $\frac{1}{2}\beta$ and the z axis is the same as the relationship in sense between the turning and advancing of the right- or left-handed. screw, according to whether the coordinates system is right- or left-handed.

 \sim Since **F** should change S to S^* and S^* to S, \mathbf{F}^2 should keep either state unchanged. Therefore it must hold that

$$
\mathbf{F}^2 = \mathbf{S} \tag{2.11}
$$

where S is a symmetry element of the crystal. In Table I all S are shown for each of the polar groups. The symbol 1 means the identity operation. 2 means the π rotation about the z axis. 4^n means the $2\pi \times (\frac{1}{4}n)$ rotation about the z axis; hence especially $4^4=1$ and $4^2=2$. 6ⁿ and 3ⁿ are analogous to 4^n . The symbol m_n means the reflection across a certain plane containing the z axis. In the point group $mm2$ there are two m_n 's;

TABLE I. The symmetry elements S of each polar group.

Polar group	Symmetry elements S	Polar group	Symmetry elements S
т 2 mm2	1. m 1.2 1, m_1 , m_2 , 2 4 ⁿ (n = 1, 2, 3, 4)	бтт 3m	4mm 4^n , m_n ($n = 1, 2, 3, 4$) 6 6^n ($n = 1, 2, \cdots, 6$) 6^n , m_n $(n=1, 2, \cdots, 6)$ $3^{n'}$ $(n=1, 2, 3)$ 3^n , m_n $(n=1, 2, 3)$

plane m_1 makes a right angle with plane m_2 . In the point group 4mm there are four m_n 's; planes m_2 , m_3 , and m_4 make angles of $\pi/4$, $2\pi/4$, and $3\pi/4$ with plane m_1 , respectively. The symbols m_n in the point groups 6mm and 3m are analogous to m_n 's in the point group 4mm. In the point group m there is only one m_n , so that the symbol m without subscript is used.

We must solve Eq. (2.11) for each polar group. First of all, noticing that every polar group possesses the identity element 1, we solve (2.11) for $S=1$. The result is that there are three solutions in all:

$$
\mathbf{F} = \mathbf{F}_{-}(\pi), \quad \mathbf{F}_{-}(0), \quad \mathbf{F}_{+}(\beta)
$$

where the value of β is arbitrary. $\mathbf{F}_{-}(\pi)$, $\mathbf{F}_{-}(0)$, and $\mathbf{F}_{+}(\beta)$ are, respectively, the inversion across the origin, the reflection across the xy plane, and the π rotation about a certain axis that lies on the xy plane. These three solutions are common to all polar groups. We next consider each individual polar group.

Let us begin with the point group 2. For $S=2$ there are two solutions:

$$
F = F_-(\frac{1}{2}\pi), \quad F_-(-\frac{1}{2}\pi).
$$

It may be obvious that in the point group ² these two solutions are equivalent:

$$
F_{-}(\frac{1}{2}\pi)\!\sim\!F_{-}(-\frac{1}{2}\pi).
$$

(The state obtained by performing $\mathbf{F}(\frac{1}{2}\pi)$ upon one state S is the same as the state obtained by performing $\mathbf{F}_{-}(-\frac{1}{2}\pi)$ upon S.) In this point group, $\mathbf{F}_{-}(0)$ and $\mathbf{F}_{-}(\pi)$ are also equivalent:

$$
\mathbf{F}_{-}(0)\!\sim\!\mathbf{F}_{-}(\pi).
$$

But any two of $F(0)$, $F(\frac{1}{2}\pi)$, and $F_+(\beta)$ are not equivalent. Therefore three different types of state transition are conceivable. The ferroelectrics of $\mathbf{F}_{-}(0)$ type, however, are considered to be nothing but the regular ferroelectrics of the kind r2. (In our present way of reasoning it is natural that the regular ferroelectrics should mix in.) Consequently, in the point group 2, two irregular kinds are anticipated; we agree to denote the kind of $F_{-}(\frac{1}{2}\pi)$ type by $i\overline{2}$ -I and the kind of $\mathbf{F}_{+}(\beta)$ type by i2-II. (The prefix "i" means "irregular.") In the latter kind the value of β depends on the choice of the x axis; it may also depend on temperature. (The value of β might depend on the shape of the crystal plate or of the electrodes.) Ferroelectric Rochelle salt is presumed to belong to the kind i2-II.

We next consider the point group $mm2$. The solutions of Eq. (2.11) for $S=2$ are

$$
F = F_-(\frac{1}{2}\pi), \quad F_-(-\frac{1}{2}\pi),
$$

as have been obtained in the point group 2. There is no solution for $S = m_1$, m_2 ; this may easily be understood if it is noticed that

$$
det m_1 = det m_2 = -1,
$$

$$
\det F^2 = (\det F)^2 = +1.
$$

We take the x axis (and hence the y axis also) perpendicular to one of the mirror planes of symmetry. In the point group $mm2$, from the requirement of symmetry, a permissible $\mathbf{F}_{+}(\beta)$ must satisfy

$$
\mathbf{F}_{+}(\beta) \sim \mathbf{F}_{+}(-\beta); \tag{2.12}
$$

hence β is limited to

$$
\beta = -\frac{1}{2}\pi, 0, \frac{1}{2}\pi, \pi.
$$

It is found that

$$
\mathbf{F}_{-}(0) \!\sim\! \mathbf{F}_{-}(\pi) \!\sim\! \mathbf{F}_{+}(0) \!\sim\! \mathbf{F}_{+}(\pi)\,,
$$

and

$$
F_{-}(\frac{1}{2}\pi)\! \sim\! F_{-}(-\frac{1}{2}\pi)\! \sim\! F_{+}(\frac{1}{2}\pi)\! \sim\! F_{+}(-\frac{1}{2}\pi).
$$

Therefore, two different types of state transition are conceivable. The ferroelectrics of $\mathbf{F}_{-}(0)$ type, however, are considered to be nothing but the regular ferroelectrics of the kind rmm2. Consequently, in the point group mm2, only one irregular kind— $F_{-}(\frac{1}{2}\pi)$ type is anticipated; we agree to denote this kind by imm2. Ferroelectric KDP is presumed to belong to this kind.

In the point group 4, since

$$
\mathbf{F}_{-}(\alpha)\!\sim\!\mathbf{F}_{-}(\alpha+\tfrac{1}{2}\pi)\!\sim\!\mathbf{F}_{-}(\alpha-\tfrac{1}{2}\pi)
$$

for an arbitrary value of $\alpha,$ and

$$
F_+(\beta)\!\sim\!F_+(\beta\!+\!\tfrac12\pi)\!\sim\!F_+(\beta\!-\!\tfrac12\pi)
$$

for an arbitrary value of β , it is sufficient to consider α and β within the ranges

$$
-\tfrac{1}{4}\pi < \alpha \leq \tfrac{1}{4}\pi \,, \quad -\tfrac{1}{4}\pi < \beta \leq \tfrac{1}{4}\pi \,,
$$

respectively. We take the x axis perpendicular to one of the side faces of the unit-cell tetragonal prism in one state. All solutions of Eq. (2.11) are

$$
\mathbf{F} = \mathbf{F}_{-}(0), \quad \mathbf{F}_{-}(\tfrac{1}{4}\pi), \quad \mathbf{F}_{+}(0), \quad \mathbf{F}_{+}(\epsilon),
$$

where ϵ is nonzero but small. The kinds of $\mathbf{F}_{-}(0)$ and $\mathbf{F}_{+}(0)$ types are considered to be the same as the regular kinds r4-I and r4-II, respectively. The kind of $\mathbf{F}(\frac{1}{4}\pi)$ type is not considered to be possible, because the alteration (or the deviation from parallelism) in the space lattice at the state transition cannot be small. The kind of $\mathbf{F}_{+}(\epsilon)$ type is considered to be possible, if ϵ is small. Consequently, in the point group 4, only one irregular kind is anticipated; we denote this kind by i4. If a ferroelectric crystal of this kind has a phase

transformation to a paraelectric phase, it is expected that as the temperature of the crystal approaches its Curie temperature, ϵ may approach zero. [It is not considered that $\mathbf{F}_{+}(\epsilon)$ type should be impossible and must become $\mathbf{F}_{+}(0)$ type.

In the point group $4mm$, all the solutions of Eq. (2.11) are exactly the same as those in the point group 4; for, there are no solutions for $S=m_n$ (n=1, 2, 3, 4). However, when as in the point group 4, the x axis is taken perpendicular to one of the side faces of the unitcell tetragonal prism in one state, a permissible $\mathbf{F}_{+}(\beta)$ must satisfy (2.12), from the requirement of symmetry. β must therefore be

$$
\beta=0, \tfrac{1}{4}\pi.
$$

 $\mathbf{F}_{+}(\frac{1}{4}\pi)$ type is not, however, considered to be possible for the same reason as that for $\mathbf{F}(\frac{1}{4}\pi)$ type. In the point group 4mm the relation

$$
\mathbf{F}_{-}(0)\!\sim\!\mathbf{F}_{+}(0)
$$

holds. The kind of $\mathbf{F}_{(0)}$ type is considered to be the same as the regular kind $r4mm$. Thus, eventually it turns out that in the point group 4mm no irregular kind is present.

In the point group 6, since

$$
\mathrm{F}_-(\alpha){\sim}\mathrm{F}_-(\alpha{+}\tfrac13\pi){\sim}\mathrm{F}_-(\alpha{-}\tfrac13\pi)
$$

for an arbitrary value of α and

$$
\mathbf{F}_+(\beta)\!\sim\!\mathbf{F}_+(\beta\!+\!\tfrac{1}{3}\pi)\!\sim\!\mathbf{F}_+(\beta\!-\!\tfrac{1}{3}\pi)
$$

for an arbitrary value of β , it is sufficient to consider α and β within the ranges

$$
-\tfrac{1}{6}\pi < \alpha \leq \tfrac{1}{6}\pi \,, \quad -\tfrac{1}{6}\pi < \beta \leq \tfrac{1}{6}\pi \,,
$$

respectively. We take the x axis parallel or perpendicular to one of the side faces of the unit-cell hexagonal prism in one state. All solutions of (2.11) are

$$
F = F_-(0), \quad F_-(\tfrac{1}{6}\pi), \quad F_+(0), \quad F_+(\epsilon),
$$

where ϵ is nonzero but small. The kind of $\mathbf{F}_{\text{m}}(\frac{1}{6}\pi)$ type is not considered to be possible, because the alteration (or the deviation from parallelism) in the space lattice at the state transition cannot be small. The kinds of $\mathbf{F}_{-}(0)$ and $\mathbf{F}_{+}(0)$ types are considered to be nothing but the regular kinds $r6-I$ and $r6-II$, respectively. Consequently, in the point group 6, only one irregular kind— $\mathbf{F}_{+}(\epsilon)$ type—is anticipated; we denote this kind by i6. If a ferroelectric crystal of this kind has a phase transformation to a paraelectric phase, it is expected that as the temperature of the crystal approaches its Curie temperature, ^e may approach zero.

In the point group $6mm$, all the solutions of (2.11) are exactly the same as those in the point group 6, but owing to the presence of the mirror planes of symmetry a permissible $\mathbf{F}_{+}(\beta)$ must satisfy (2.12), so that β must be

$$
\beta=0, \tfrac{1}{6}\pi.
$$

(The x axis is taken in the same way as in the point

whereas

group 6.) $\mathbf{F}_{+}(\frac{1}{6}\pi)$ type is not considered to be possible, for the same reason as that for $\mathbf{F}(\frac{1}{6}\pi)$ type. The relation

$$
\mathbf{F}_{-}(0)\!\sim\!\mathbf{F}_{+}(0)
$$

holds. The kind of $F(0)$ type is considered to be nothing but the regular kind r6mm. Therefore, in the point group 6mm no irregular kind is anticipated.

In the trigonal system there are two kinds of Bravais lattices, viz., hexagonal P lattice and trigonal R lattice The x axis is taken perpendicular, in the hexagonal P lattice, to one of the side faces of the unit-cell hexagonal prism and, in the trigonal R lattice, to one of the edges of the unit-cell rhombohedron. In the point groups 3 and $3m$, the solutions of (2.11) are

$$
\mathbf{F} = \mathbf{F}_{-}(\frac{1}{3}\pi), \ \mathbf{F}_{-}(0), \ \mathbf{F}_{+}(0), \ \mathbf{F}_{+}(\epsilon), \ \mathbf{F}_{+}(\frac{1}{3}\pi), \ \mathbf{F}_{+}(\frac{1}{3}\pi + \epsilon),
$$

where ϵ is nonzero but small. $\mathbf{F}(\frac{1}{2}\pi)$ can be replaced by $\mathbf{F}_{-}(\pi)$ since

$$
\mathbf{F}_{-}(\tfrac{1}{3}\pi)\!\sim\!\mathbf{F}_{-}(\pi).
$$

In the point group 3 with the hexagonal P lattice, the kinds of $\mathbf{F}_{-}(\pi)$, $\mathbf{F}_{-}(0)$, $\mathbf{F}_{+}(0)$, and $\mathbf{F}_{+}(\frac{1}{3}\pi)$ types are considered to be nothing but the regular kinds $r3P$ -I, -II, -III, and -IV, respectively. The kinds of $\mathbf{F}_{+}(\epsilon)$ and $\mathbf{F}_{+}(\frac{1}{2}\pi+\epsilon)$ types are irregular. Thus two irregular kinds are anticipated; we denote the kind of $\mathbf{F}_{+}(\epsilon)$ type by i3P-I and the kind of $\mathbf{F}_{+}(\frac{1}{3}\pi+\epsilon)$ type by i3P-II. (As temperature approaches the Curie temperature, ϵ may approach zero.)

In the point group $3m$ with the hexagonal P lattice, a permissible $\mathbf{F}_{+}(\beta)$ must satisfy (2.12), so that β is limited to

$$
\beta=0, \, \tfrac{1}{3}\pi
$$

Either the relations

$$
\mathbf{F}_{+}(0) \sim \mathbf{F}_{-}(\pi), \quad \mathbf{F}_{+}(\frac{1}{3}\pi) \sim \mathbf{F}_{-}(0)
$$

or the relations

$$
F_+({\textstyle{\frac{1}{3}}}\pi){\sim}F_- (\pi)\,,\quad F_+(0){\sim}F_-(0)
$$

hold according to whether the mirror planes of symmetry are parallel or perpendicular to the side faces of the unit-cell hexagonal prism. The kinds of $F_{-(\pi)}$ and $\mathbf{F}_{-}(0)$ types are considered to be the same as the regular kinds $r3mP$ -I and $r3mP$ -II, respectively. Therefore no irregular kind is present.

In the point group 3 with the trigonal R lattice, the kinds of $\mathbf{F}_{-}(0)$, $\mathbf{F}_{+}(\frac{1}{3}\pi)$, and $\mathbf{F}_{+}(\frac{1}{3}\pi+\epsilon)$ types are not considered to be possible, because the alteration in the space lattice at the state transition cannot be small. The kinds of $\mathbf{F}_{-}(\pi)$ and $\mathbf{F}_{+}(0)$ types are considered to be the same as the regular kinds $r3R$ -I and $r3R$ -II. Therefore only one irregular kind— $F_+(\epsilon)$ type—is present; we denote this kind by i3R.

In the point group $3m$ with the trigonal R lattice, only one kind— $\mathbf{F}_{-}(\pi)$ type—is conceivable. This kind is, however, considered to be the same as the regular kind $r3mR$. Therefore no irregular kind is present.

The point groups 1 and *m* yet remain to be examined.

TABLE II. The type of state transition of each kind of irregular ferroelectric.

Irregular kind	Type of state transition
$i1-I$	Reflection
$i1$ -II	Rotation
im	Reflection, rotation ^a
$i2-I$	Rotatory reflection
$i2$ -II	Rotationb
imm2	Rotatory reflection, rotation ^o
i4	Rotation ^d
ż6	Rotation [®]
i3R	Rotation ^f
$i3P-I$	Rotation ^g
$i3P$ -II	Rotation ^h

a There is only one rotation axis. This is parallel to the mirror plane of symmetry. ^b There are two equivalent rotation axes which are perpendicular to each

other.

There are two equivalent rotation axes. Each of these makes an angle

of $\frac{1}{4}\pi$ with each of the mirror planes of symmetry.

d'There are four equivalent rotation axes any two adjoining of which

d'There are fo

In these the ferroelectric direction—the z axis—is crystallographically indefinite and may vary with temperature. (It is only definite that in m the ferroelectric direction should be parallel to the mirror plane of symmetry.) The solutions of Eq. (2.11) are the same in 1 and m; they are

$$
F = F_-(\pi), F_-(0), F_+(\beta).
$$

In the point group 1 the kind of $F_-(\pi)$ type is considered to be the same as the regular kind $r1$. Therefore two irregular kinds are conceivable; we denote the kind of $\mathbf{F}_{-}(0)$ type by i1-I and the kind of $\mathbf{F}_{+}(\beta)$ type by *i*1-II. The value of β depends on the choice of the x axis and also may depend on temperature.

In the point group m , when the y axis is taken perpendicular to the mirror plane of symmetry, a permissible $\mathbf{F}_{+}(\beta)$ must satisfy (2.12), so that β is limited to

$$
\beta\!=\!0,\,\pi\,.
$$

The relations

$$
F_{+}(\pi)\!\sim\!F_{-}(\pi)\,,\ \ \, F_{+}(0)\!\sim\!F_{-}(0)
$$

hold. The kind of $\mathbf{F}(\pi)$ type is considered to be the same as the regular kind rm. Therefore only one irregular kind— $\mathbf{F}_{-}(0)$ type—is conceivable; we denote this kind by im.

Now we have finished examining all polar groups. It is seen that the irregular ferroelectrics are divided into 11 kinds in accordance with their point groups, Bravais lattices, and types of state transition. The symbols for these 11 kinds and their types of state

Regular kind	Type of state transition
r1	Inversion
rm	Inversion, rotation ^a
12	Inversion, reflection
rmm2	Inversion, reflection, rotation ^b
$r4$ -T	Inversion, reflection
$r4$ -TT	Rotation ^o
r4mm	Inversion, reflection, rotation ^o
$r6-I$	Inversion, reflection
$r6$ -II	Rotation ^d
r6mm	Inversion, reflection, rotation ^d
$r3R$ -T	Inversion
$r3R$ -II	Rotation [®]
r3mR	Inversion, rotation [®]
$r3P-I$	Inversion
$r3P$ -II	Reflection
$r3P$ -III	Rotationf
$r3P$ -IV	Rotation ⁸
$r3mP-I$	Inversion, rotation ^h
$r3mP$ -II	Reflection, rotation ⁱ

TABLE III. The type of state transition of each kind

a There is only one rotation axis. This is perpendicular to the mirror plane of symmetry. There are two equivalent rotation axes. Each of these is perpendicular (or parallel) to one of the mirror planes of symmetry. There

unit-cell hexagonal prism.
 s There are three equivalent rotation axes any two of which make an angle of $\frac{1}{3}\pi$. Each of them is parallel to one of the side faces of the unit-cell

hexagonal prism.

h There are three equivalent rotation axes any two of which make an
angle of $\frac{1}{3}\pi$. Each of them is perpendicular to one of the mirror planes of symmetry
i There

There are three equivalent rotation axes any two of which make an angle of $\frac{1}{3}\pi$. Each of them is parallel to one of the mirror planes of symmetry.

transition are collectively shown in Table II. There are no irregular ferroelectrics belonging to the point groups 4mm, 6mm, and 3m; or in other words, the ferroelectrics belonging to these point groups are all regular. In the irregular ferroelectrics there are three types of state transition, viz. , reflection type, rotatory-reflection type, and rotation type. Reflection type is such that one of the two stable states of the crystal plate is obtained by performing upon the other a reflection operation across a plane perpendicular to the ferroelectric direction. Rotatory-reflection type is such that one of the two stable states of the crystal plate is obtained by performing upon the other a $\frac{1}{2}\pi$ rotation about the ferroelectric direction followed by a reflection across a plane perpendicular to the ferroelectric direction. (The order of the reflection and the $\frac{1}{2}\pi$ rotation is immaterial.) This type may as well be termed rotatory-inversion type. Rotation type is such that one of the two stable states of the crystal plate is obtained by performing upon the other a π rotation about a certain axis perpendicular to the ferroelectric direction.

We incidentally tabulate, in Table III, the symbols for the 19 kinds of regular ferroelectrics and their types of state transition. There are three types of state transition —inversion type, reflection type, and rotation type.¹ Inversion type, the state of the two stable states of the *crystal* (not *crystal plate*) is obtained by performing upon the other an inversion across a point. Reflection type is such that one of the two stable states of the crystal is obtained by performing upon the other a reflection across a plane perpendicular to the *direction* of the spontaneous polarization vector (not ferroelectric direction). Rotation type is such that one of the two stable states of the crystal is obtained by performing upon the other a π rotation about a certain axis perpendicular to the direction of the spontaneous polarization vector.

In rotation type, whether regular or irregular, a variety occurs according to difference in the direction of the rotation axis. In Tables II and III we have specified the total number of the rotation axes equivalent to one another and their direction.

3. FERROELECTRIC TRANSFORMATIONS OF TENSORIAL PROPERTIES IN IRREGULAR FERROELECTRICS

3.1. Preliminary Remarks

We shall show in the subsequent three subsections how the tensorial properties of the irregular ferroelectric crystal-plates should be changed with the state transition. We give the results alone. (An illustration of proof is given in Sec. 3.¹ of Ref. 5.) In Sec. 3.2 the polar and axial tensors of rank two are considered. These need not be symmetric. In Sec. 3.3 the polar and axial tensors of rank three are considered. These are assumed to be partially symmetric, i.e., to be such that assumed to be partially symmetric, i.e., to be such that
their (i,j,k) element T_{ijk} is equal to their (i,k,j) element T_{ikj} . (A tensor such that $T_{ijk} = T_{jik}$ can be translate \sum_{i}^{T} \sum_{i}^{T} (A tensor such that $T_{ijk} = T_{ikj}$.) In Sec. 3.4 the polarities and axial tensors of rank four are considered. These are assumed to be such that $T_{i/kl} = T_{jkl} = T_{i,lkl}$. In order to represent the tensors by matrices, we replace a commutable double suffix by a single suffix:

$$
11 \rightarrow 1, \quad 22 \rightarrow 2, \quad 33 \rightarrow 3, \quad 23 \text{ and } 32 \rightarrow 4,
$$

$$
31 \text{ and } 13 \rightarrow 5, \quad 12 \text{ and } 21 \rightarrow 6.
$$

A set of rectangular coordinate axes x , y , z is taken with the s axis parallel to the ferroelectric direction. These axes are spatially fixed and independent of the state transition. In the kind im the y axis is taken perpendicular to the mirror plane of symmetry. In the kind $\lim_{m \to \infty}$ the x axis (and hence the y axis also) is taken perpendicular to one of the mirror planes of symmetry. There is a case that the value of every element of a tensor is independent of the choice of the x axis (as long as the x axis is perpendicular to the z axis). In this case we say simply, "the direction of the x axis is free."

In the irregular ferroelectrics of rotation type, as has been seen in Sec. 2, one of their two stable states is obtained by performing upon the other a π rotation about a certain axis perpendicular to the ferroelectric direction. The symbol β appearing below means twice the angle made by this rotation axis with the x axis (i.e., means the same as in Sec. 2).

3.2. Polar and Axial Tensors of Rank Two

In the kinds $i1$ -I and $i1$ -II, the polar or axial tensor in one state is

$$
\begin{bmatrix} T_{11} & T_{12} & T_{13} \ T_{21} & T_{22} & T_{23} \ T_{31} & T_{32} & T_{33} \end{bmatrix} . \tag{3.1}
$$

In i1-I this tensor is changed, if polar, to

$$
\begin{bmatrix} T_{11} & T_{12} - T_{13} \ T_{21} & T_{22} - T_{23} \ -T_{31} - T_{32} & T_{33} \end{bmatrix}
$$

and, if axial, to

$$
\begin{bmatrix} -T_{11} - T_{12} & T_{13} \ -T_{21} - T_{22} & T_{23} \ T_{31} & T_{32} - T_{33} \end{bmatrix}.
$$

 $\overline{ }$ In *i*1-II the tensor (3.1) is changed, whether polar or $\begin{bmatrix} T_{21} & T_{22} & 0 \ 0 & 0 & T_{33} \end{bmatrix}$

$$
\begin{bmatrix} T'_{11} & T'_{12} & T'_{13} \\ T'_{21} & T'_{22} & T'_{23} \\ T'_{31} & T'_{32} & T'_{33} \end{bmatrix},
$$

where

 $T'{}_{33} = T{}_{33}$.

$$
T'_{11} = T_{11}(\cos\beta)^2 + T_{22}(\sin\beta)^2
$$

\n
$$
+ (T_{12} + T_{21}) \cos\beta \sin\beta,
$$

\n
$$
T'_{22} = T_{11}(\sin\beta)^2 + T_{22}(\cos\beta)^2
$$

\n
$$
- (T_{12} + T_{21}) \cos\beta \sin\beta,
$$

\n
$$
T'_{12} = (T_{11} - T_{22}) \cos\beta \sin\beta - T_{12}(\cos\beta)^2
$$

\n
$$
+ T_{21}(\sin\beta)^2,
$$

\n
$$
T'_{21} = (T_{11} - T_{22}) \cos\beta \sin\beta + T_{12}(\sin\beta)^2
$$

\n
$$
- T_{21}(\cos\beta)^2,
$$

\n
$$
T'_{13} = - T_{13} \cos\beta - T_{23} \sin\beta,
$$

\n
$$
T'_{23} = - T_{13} \sin\beta + T_{23} \cos\beta,
$$

\n
$$
T'_{31} = - T_{31} \cos\beta - T_{32} \sin\beta,
$$

\n
$$
T'_{32} = - T_{31} \sin\beta + T_{32} \cos\beta,
$$

Especially, if the x axis is taken parallel to the rotation axis, the tensor (3.1) is changed to

$$
\begin{bmatrix} T_{11} - T_{12} - T_{13} \ -T_{21} & T_{22} & T_{23} \ -T_{31} & T_{32} & T_{33} \end{bmatrix}.
$$

If, instead of the x axis, the y axis is taken parallel to the rotation axis, the tensor (3.1) is changed to

$$
\begin{bmatrix} T_{11} - T_{12} & T_{13} \ -T_{21} & T_{22} - T_{23} \ T_{31} - T_{32} & T_{33} \end{bmatrix}.
$$

In the kind im the polar tensor in one state is

$$
\begin{bmatrix} T_{11} & 0 & T_{13} \\ 0 & T_{22} & 0 \\ T_{31} & 0 & T_{33} \end{bmatrix}.
$$

This is changed to

$$
\begin{bmatrix} T_{11} & 0 & -T_{13} \\ 0 & T_{22} & 0 \\ -T_{31} & 0 & T_{33} \end{bmatrix}.
$$

(3.1) The axial tensor in one state is
 $\begin{bmatrix} 0 & T_{12} & 0 \end{bmatrix}$

$$
\begin{bmatrix} 0 & T_{12} & 0 \ T_{21} & 0 & T_{23} \ 0 & T_{32} & 0 \end{bmatrix}.
$$

This is changed to

$$
\begin{bmatrix} 0 & -T_{12} & 0 \\ -T_{21} & 0 & T_{23} \\ 0 & T_{32} & 0 \end{bmatrix}
$$

In the kinds i2-I and i2-II, the polar or axial tensor in one state is

$$
\begin{bmatrix} T_{11} & T_{12} & 0 \\ T_{21} & T_{22} & 0 \\ 0 & 0 & T_{33} \end{bmatrix}.
$$
 (3.3)

In i2-I this tensor is changed, if polar, to

$$
\begin{bmatrix} T_{22} - T_{21} & 0 \ -T_{12} & T_{11} & 0 \ 0 & 0 & T_{33} \end{bmatrix}
$$

$$
\begin{bmatrix} -T_{22} & T_{21} & 0 \ T_{12} - T_{11} & 0 \end{bmatrix}.
$$

and if axial, to

$$
\left[\begin{array}{cc} T_{12}-T_{11}&0\\0&0-T_{33}\end{array}\right]\cdot
$$

In $i2$ -II the tensor (3.3) is changed, whether polar or axial, to

$$
\begin{bmatrix} T'{}_{11} & T'{}_{12} & 0 \\ T'{}_{21} & T'{}_{22} & 0 \\ 0 & 0 & T'{}_{33} \end{bmatrix},
$$

where nonzero elements T'_{11} , etc., are given by (3.2). Especially if the x axis (and hence the y axis also) is taken parallel to one of the rotation axes, the tensor (3.3) is changed to

$$
\begin{bmatrix} T_{11} - T_{12} & 0 \ -T_{21} & T_{22} & 0 \ 0 & 0 & T_{33} \end{bmatrix}
$$

In the kind $imm2$ the polar tensor in one state is

$$
\begin{bmatrix} T_{11} & 0 & 0 \\ 0 & T_{22} & 0 \\ 0 & 0 & T_{33} \end{bmatrix}
$$

This is changed to

$$
\begin{bmatrix} T_{22} & 0 & 0 \ 0 & T_{11} & 0 \ 0 & 0 & T_{33} \end{bmatrix}.
$$

The axial tensor in one state is

$$
\begin{bmatrix}0&T_{12}&0\\T_{21}&0&0\\0&0&0\end{bmatrix}
$$

This is changed to

$$
\begin{bmatrix} 0 & T_{21} & 0 \ T_{12} & 0 & 0 \ 0 & 0 & 0 \end{bmatrix}
$$

In the kinds $i4$, $i6$, $i3R$, $i3P-I$, and $i3P-II$, the polar or axial tensor in one state is

$$
\begin{bmatrix} a & c & 0 \\ -c & a & 0 \\ 0 & 0 & b \end{bmatrix}
$$

(The direction of the x axis is free.) This is changed, whether polar or axial, to

$$
\begin{bmatrix} a & -c & 0 \ c & a & 0 \ 0 & 0 & b \end{bmatrix}
$$

3.3. Polar and Axial Tensors of Rank Three

In the kinds i1-I and i1-II, the polar or axial tensor in one state is

$$
\begin{bmatrix} T_{11} & T_{12} & T_{13} & T_{14} & T_{15} & T_{16} \ T_{21} & T_{22} & T_{23} & T_{24} & T_{25} & T_{26} \ T_{31} & T_{32} & T_{33} & T_{34} & T_{35} & T_{36} \end{bmatrix}.
$$
 (3.4)

In i1-I this tensor is changed, if polar, to

$$
\left[\begin{array}{ccc}T_{11}& T_{12}& T_{13}-T_{14}-T_{15}&T_{16}\\T_{21}& T_{22}& T_{23}-T_{24}-T_{25}&T_{26}\\-T_{31}-T_{32}-T_{33}& T_{34}& T_{35}-T_{36}\end{array}\right]
$$

and, if axial, to

$$
\begin{bmatrix} -\,T_{11}-T_{12}-T_{13} & T_{14} & T_{15}-T_{16} \\ -\,T_{21}-T_{22}-T_{23} & T_{24} & T_{25}-T_{26} \\ T_{31} & T_{32} & T_{33}-T_{34}-T_{35} & T_{36} \end{bmatrix} \, .
$$

In $i1$ -II the tensor (3.4) is changed, whether polar or axial, to

$$
\begin{bmatrix} T'{}_{11} & T'{}_{12} & T'{}_{13} & T'{}_{14} & T'{}_{15} & T'{}_{16} \\ T'{}_{21} & T'{}_{22} & T'{}_{23} & T'{}_{24} & T'{}_{25} & T'{}_{26} \\ T'{}_{31} & T'{}_{32} & T'{}_{33} & T'{}_{34} & T'{}_{35} & T'{}_{36} \end{bmatrix},
$$

where

 $T'_{11} = T_{11}(\cos\beta)^3 + T_{22}(\sin\beta)^3$ $+T_{12} \cos\beta(\sin\beta)^2 + T_{21}(\cos\beta)^2 \sin\beta$ $+T_{16} \cos\beta \sin 2\beta + T_{26} \sin\beta \sin 2\beta$, $T'_{22} = T_{11}(\sin\!\beta)^3 - T_{22}(\cos\!\beta)^3$ + $T_{12}(\cos\beta)^2 \sin\beta - T_{21} \cos\beta(\sin\beta)^2$
- $T_{16} \sin\beta \sin2\beta + T_{26} \cos\beta \sin2\beta$, $T'_{12}=T_{11}\cos\beta(\sin\beta)^2+T_{22}(\cos\beta)^2\sin\beta$

+
$$
T_{12}(\cos\beta)^3 + T_{21}(\sin\beta)^3 - T_{16}\cos\beta\sin2\beta - T_{26}\sin\beta\sin2\beta,
$$

 $T'_{21} = T_{11}(\cos\beta)^2 \sin\beta - T_{22} \cos\beta(\sin\beta)^2$ $+T_{12}(\sin\!\beta)^3 - T_{21}(\cos\!\beta)^3$ $+T_{16} \sin\beta \sin 2\beta - T_{26} \cos\beta \sin 2\beta$, $T'_{16} = T_{11} (\cos\beta)^2 \sin\beta - T_{22} \cos\beta (\sin\beta)^2$
- $T_{12} (\cos\beta)^2 \sin\beta + T_{21} \cos\beta (\sin\beta)^2$
- $T_{16} \cos\beta \cos2\beta - T_{26} \sin\beta \cos2\beta$, $T'_{26} = T_{11} \cos\beta(\sin\beta)^2 + T_{22}(\cos\beta)^2 \sin\beta$
- $T_{12} \cos\beta(\sin\beta)^2 - T_{21}(\cos\beta)^2 \sin\beta$ $-T_{16}$ sin β cos2 β + T_{26} cos β cos2 β , (3.5) $T'_{14} = T_{14} (\cos\beta)^2 - T_{25} (\sin\beta)^2$ $+(T_{24}-T_{15})\cos\beta\sin\beta$, $T'_{25} = -T_{14}(\sin\beta)^2 + T_{25}(\cos\beta)^2$ $+(T_{24}-T_{15}) \cos\beta \sin\beta$, $T'_{15} = -(T_{14}+T_{25}) \cos\beta \sin\beta - T_{15}(\cos\beta)^2$
- $T_{24}(\sin\beta)^2$, $T'_{24} = (T_{14}+T_{25}) \cos\beta \sin\beta - T_{15}(\sin\beta)^2$
- $T_{24}(\cos\beta)^2$, $T'_{31} = -T_{31}(\cos\beta)^2 - T_{32}(\sin\beta)^2 - T_{36} \sin 2\beta$, $T'_{32} = -T_{31}(\sin\beta)^2 - T_{32}(\cos\beta)^2 + T_{36} \sin 2\beta$, $T'_{36} = (T_{32} - T_{31}) \cos\beta \sin\beta + T_{36} \cos2\beta$, $T'_{13}= T_{13} \cos\beta + T_{23} \sin\beta$, $T'_{23}= T_{13} \sin \beta - T_{23} \cos \beta$, $T'_{34} = -T_{34} \cos\beta + T_{35} \sin\beta$, $T'_{35} = T_{34} \sin{\beta} + T_{35} \cos{\beta}$, $T'_{33} = -T_{33}$.

Expecially if the x axis is taken parallel to the rotation axis, the tensor (3.4) is changed to

$$
\begin{bmatrix} T_{11} & T_{12} & T_{13} & T_{14} - T_{15} - T_{16} \\ -T_{21} - T_{22} - T_{23} - T_{24} & T_{25} & T_{26} \\ -T_{31} - T_{32} - T_{33} - T_{34} & T_{35} & T_{36} \end{bmatrix}
$$

If, instead of the x axis, the y axis is taken parallel to the rotation axis, the tensor (3.4) is changed to

$$
\begin{bmatrix} -T_{11} - T_{12} - T_{13} & T_{14} - T_{15} & T_{16} \\ T_{21} & T_{22} & T_{23} - T_{24} & T_{25} - T_{26} \\ -T_{31} - T_{32} - T_{33} & T_{34} - T_{35} & T_{36} \end{bmatrix}.
$$

In the kind im the polar tensor in one state is

$$
\left[\begin{matrix} T_{11} & T_{12} & T_{13} & 0 & T_{15} & 0 \\ 0 & 0 & 0 & T_{24} & 0 & T_{26} \\ T_{31} & T_{32} & T_{33} & 0 & T_{35} & 0 \end{matrix}\right].
$$

This is changed to

$$
\begin{bmatrix} T_{11} & T_{12} & T_{13} & 0 & -T_{15} & 0 \ 0 & 0 & 0 & -T_{24} & 0 & T_{26} \ -T_{31} - T_{32} - T_{33} & 0 & T_{35} & 0 \end{bmatrix}.
$$

The axial tensor in one state is

This is changed to

$$
\begin{bmatrix} 0 & 0 & 0 & T_{14} & 0 & -T_{16} \\ -T_{21} & -T_{22} & -T_{23} & 0 & T_{25} & 0 \\ 0 & 0 & 0 & -T_{34} & 0 & T_{36} \end{bmatrix}.
$$

In the kinds i2-I and i2-II, the polar or axial tensor (The direction of the x axis is free.) This is changed, in one state is

$$
\begin{bmatrix} 0 & 0 & 0 & T_{14} & T_{15} & 0 \ 0 & 0 & 0 & T_{24} & T_{25} & 0 \ T_{31} & T_{32} & T_{33} & 0 & 0 & T_{36} \end{bmatrix}.
$$
 (3.6)

In i2-I this tensor is changed, if polar, to

$$
\begin{bmatrix} 0 & 0 & 0 & T_{25} - T_{24} & 0 \\ 0 & 0 & 0 & -T_{15} & T_{14} & 0 \\ -T_{32} - T_{31} - T_{33} & 0 & 0 & T_{36} \end{bmatrix}
$$

and, if axial, to

$$
\begin{bmatrix} 0 & 0 & 0 & -T_{25} & T_{24} & 0 \\ 0 & 0 & 0 & T_{15} - T_{14} & 0 \\ T_{32} & T_{31} & T_{33} & 0 & 0 & -T_{36} \end{bmatrix}.
$$

In $i2$ -II the tensor (3.6) is changed, whether polar or axial, to

$$
\begin{bmatrix} 0 & 0 & 0 & T'_{14} & T'_{15} & 0 \\ 0 & 0 & 0 & T'_{24} & T'_{25} & 0 \\ T'_{31} & T'_{32} & T'_{33} & 0 & 0 & T'_{36} \end{bmatrix},
$$

where nonzero elements T'_{14} , etc., are given by (3.5). Expecially, if the x axis (and hence the y axis also) is taken parallel to one of the rotation axes, the tensor (3.6) is changed to

$$
\begin{bmatrix} 0 & 0 & 0 & T_{14} - T_{15} & 0 \\ 0 & 0 & 0 & -T_{24} & T_{25} & 0 \\ -T_{31} - T_{32} - T_{33} & 0 & 0 & T_{36} \end{bmatrix}.
$$

In the kind \imath mm2 the polar tensor in one state is

$$
\begin{bmatrix} 0 & 0 & 0 & 0 & T_{15} & 0 \\ 0 & 0 & 0 & T_{24} & 0 & 0 \\ T_{31} & T_{32} & T_{33} & 0 & 0 & 0 \end{bmatrix}.
$$

This is changed to

$$
\begin{bmatrix} 0 & 0 & 0 & 0 & -T_{24} & 0 \ 0 & 0 & 0 & -T_{15} & 0 & 0 \ -T_{32} & -T_{31} & -T_{33} & 0 & 0 & 0 \end{bmatrix}
$$

The axial tensor in one state is

$$
\begin{bmatrix} 0 & 0 & 0 & T_{14} & 0 & 0 \ 0 & 0 & 0 & 0 & T_{25} & 0 \ 0 & 0 & 0 & 0 & 0 & T_{36} \end{bmatrix}.
$$

This is changed to

In the kinds i4 and i6, the polar or axial tensor in

one state is

$$
\begin{bmatrix} 0 & 0 & 0 & d & c & 0 \\ 0 & 0 & 0 & c & -d & 0 \\ b & b & a & 0 & 0 & 0 \end{bmatrix}.
$$

whether polar or axial, to

In the kinds $i3R$, $i3P-I$, and $i3P-II$, the polar or axial tensor in one state is

$$
\begin{bmatrix} -e & e & 0 & d & c & f \\ f & -f & 0 & c & -d & e \\ b & b & a & 0 & 0 & 0 \end{bmatrix}.
$$
 (3.7)

This is changed, whether polar or axial, to

$$
\begin{bmatrix} -e' & e' & 0 & d & -c & f' \\ f' & -f' & 0 & -c & -d & e' \\ -b & -b & -a & 0 & 0 & 0 \end{bmatrix}
$$

where

$$
e' = e \cos 3\beta - f \sin 3\beta
$$
, $f' = -e \sin 3\beta - f \cos 3\beta$.

Therefore, especially if the x axis is taken parallel to one of the rotation axes, the tensor (3.7) is changed to

$$
\begin{bmatrix} -e & e & 0 & d & -c & -f \\ -f & f & 0 & -c & -d & e \\ -b & -b & -a & 0 & 0 & 0 \end{bmatrix}.
$$

If, instead of the x axis, the y axis is taken parallel to one of the rotation axes, the tensor (3.7) is changed to

$$
\begin{bmatrix} e & -e & 0 & d & -c & f \\ f & -f & 0 & -c & -d & -e \\ -b & -b & -a & 0 & 0 & 0 \end{bmatrix}.
$$

3.4. Polar and Axial Tensors of Rank Four

In the kinds i1-I and i1-II, the polar or axial tensor in one state is

$$
\begin{bmatrix}\nT_{11} & T_{12} & T_{13} & T_{14} & T_{15} & T_{16} \\
T_{21} & T_{22} & T_{23} & T_{24} & T_{25} & T_{26} \\
T_{31} & T_{32} & T_{33} & T_{34} & T_{35} & T_{36} \\
T_{41} & T_{42} & T_{43} & T_{44} & T_{45} & T_{46} \\
T_{51} & T_{52} & T_{53} & T_{54} & T_{55} & T_{56} \\
T_{61} & T_{62} & T_{63} & T_{64} & T_{65} & T_{66}\n\end{bmatrix}.
$$
\n(3.8)

In *i*1-I this tensor is changed, if polar, to

and, if axial, to

$$
\begin{bmatrix} -T_{11} - T_{12} - T_{13} & T_{14} & T_{15} - T_{16} \ -T_{21} - T_{22} - T_{23} & T_{24} & T_{25} - T_{26} \ -T_{31} - T_{32} - T_{33} & T_{34} & T_{35} - T_{36} \ T_{41} & T_{42} & T_{43} - T_{44} - T_{45} & T_{46} \ T_{51} & T_{52} & T_{53} - T_{54} - T_{55} & T_{56} \ -T_{61} - T_{62} - T_{63} & T_{64} & T_{65} - T_{66} \end{bmatrix}.
$$

In $i1$ -II, if the x axis is taken parallel to the rotation axis, the tensor (3.8) is changed, whether polar or In i2-I this tensor is changed, if polar, to axial, to

 T_{11} $T_{\rm 21}$ $T{\scriptstyle_{31}}$ $T_{\rm 41}$ $T_{\,\mathrm{51}}$ $T_{\bf 61}$ $T{\rm_{12}}$ $T{\rm_{22}}$ $T{\rm_{32}}$ $\frac{T_{42}}{-T_{52}}$ $T_{\,62}$ $T_{\rm 16}$ $T_{\rm 26}$ $T_{\,36}$ $T_{\rm~46}$ $T_{\,\mathrm{56}}$ $T_{\,\rm 66}$ $T_{\rm 15}$ $T{\scriptstyle_{25}}$ $T_{\,\rm 35}$ $T_{\rm~45}$ $T{\scriptstyle_{55}}$ $T_{\,65}$ $T{\scriptstyle_{13}}$ $T_{\,23}$ $T_{\,33}$ $T_{\rm~43}$ $T{\rm_{53}}$ $T_{\rm~63}$ $T_{\rm\,14}$ $T_{\ 24}$ $T_{\ 34}$ $T_{\rm~44}$ $T_{\,\mathrm{54}}$ $T_{\rm \,64}$

If instead of the x axis, the y axis is taken parallel to the rotation axis, the tensor (3.8) is changed to

$$
\left[\begin{array}{cccccc} T_{11} & T_{12} & T_{13} - T_{14} & T_{15} - T_{16} \\ T_{21} & T_{22} & T_{23} - T_{24} & T_{25} - T_{26} \\ T_{31} & T_{32} & T_{33} - T_{34} & T_{35} - T_{36} \\ -T_{41} - T_{42} - T_{43} & T_{44} - T_{45} & T_{46} \\ T_{51} & T_{52} & T_{53} - T_{54} & T_{55} - T_{56} \\ -T_{61} - T_{62} - T_{63} & T_{64} - T_{65} & T_{66} \end{array}\right]
$$

In the kind *im* the polar tensor in one state is

$$
\begin{bmatrix} T_{11} & T_{12} & T_{13} & 0 & T_{15} & 0 \ T_{21} & T_{22} & T_{23} & 0 & T_{25} & 0 \ T_{31} & T_{32} & T_{33} & 0 & T_{35} & 0 \ 0 & 0 & 0 & T_{44} & 0 & T_{46} \ T_{51} & T_{52} & T_{53} & 0 & T_{55} & 0 \ 0 & 0 & 0 & T_{64} & 0 & T_{66} \end{bmatrix}.
$$

This is changed to

$$
\begin{bmatrix}\nT_{11} & T_{12} & T_{13} & 0 & -T_{15} & 0 \\
T_{21} & T_{22} & T_{23} & 0 & -T_{25} & 0 \\
T_{31} & T_{32} & T_{33} & 0 & -T_{35} & 0 \\
0 & 0 & 0 & T_{44} & 0 & -T_{46} \\
-T_{51} - T_{52} - T_{53} & 0 & T_{55} & 0 \\
0 & 0 & 0 & -T_{64} & 0 & T_{66}\n\end{bmatrix}.
$$

The axial tensor in one state is

$$
\begin{bmatrix} 0 & 0 & 0 & T_{14} & 0 & T_{16} \\ 0 & 0 & 0 & T_{24} & 0 & T_{26} \\ 0 & 0 & 0 & T_{34} & 0 & T_{36} \\ T_{41} & T_{42} & T_{43} & 0 & T_{45} & 0 \\ 0 & 0 & 0 & T_{54} & 0 & T_{56} \\ T_{61} & T_{62} & T_{63} & 0 & T_{65} & 0 \end{bmatrix}.
$$

This is changed to

$$
\begin{bmatrix}\n0 & 0 & 0 & T_{14} & 0 & -T_{16} \\
0 & 0 & 0 & T_{24} & 0 & -T_{26} \\
0 & 0 & 0 & T_{34} & 0 & -T_{36} \\
T_{41} & T_{42} & T_{43} & 0 & -T_{45} & 0 \\
0 & 0 & 0 & -T_{54} & 0 & T_{56} \\
-T_{61} - T_{62} - T_{63} & 0 & T_{65} & 0\n\end{bmatrix}
$$

In the kinds $i2$ -I and $i2$ -II, the polar or axial tensor in one state is

$$
\begin{bmatrix}\nT_{11} & T_{12} & T_{13} & 0 & 0 & T_{16} \\
T_{21} & T_{22} & T_{23} & 0 & 0 & T_{26} \\
T_{31} & T_{32} & T_{33} & 0 & 0 & T_{36} \\
0 & 0 & 0 & T_{44} & T_{45} & 0 \\
0 & 0 & 0 & T_{54} & T_{55} & 0 \\
T_{61} & T_{62} & T_{63} & 0 & 0 & T_{66}\n\end{bmatrix}.
$$
\n(3.9)

$$
\left[\begin{array}{cccccc}T_{22}&T_{21}&T_{23}&0&0&-T_{26}\\T_{12}&T_{11}&T_{13}&0&0&-T_{16}\\T_{32}&T_{31}&T_{33}&0&0&-T_{36}\\0&0&0&T_{55}-T_{54}&0\\0&0&0&-T_{45}&T_{44}&0\\-T_{62}-T_{61}-T_{63}&0&0&T_{66}\end{array}\right]
$$

and if axial, to

$$
\begin{bmatrix} -T_{22} - T_{21} - T_{23} & 0 & 0 & T_{26} \\ -T_{12} - T_{11} - T_{13} & 0 & 0 & T_{16} \\ -T_{32} - T_{31} - T_{33} & 0 & 0 & T_{36} \\ 0 & 0 & 0 & -T_{55} & T_{54} & 0 \\ 0 & 0 & 0 & T_{45} - T_{44} & 0 \\ T_{62} & T_{61} & T_{63} & 0 & 0 & -T_{66} \end{bmatrix}
$$

In $i2$ -II, if the x axis (and hence the y axis also) is taken parallel to one of the rotation axes, the tensor (3.9) is changed, whether polar or axial, to

$$
\begin{bmatrix}\nT_{11} & T_{12} & T_{13} & 0 & 0 & -T_{16} \\
T_{21} & T_{22} & T_{23} & 0 & 0 & -T_{26} \\
T_{31} & T_{32} & T_{33} & 0 & 0 & -T_{36} \\
0 & 0 & 0 & T_{44} - T_{45} & 0 \\
0 & 0 & 0 & -T_{54} & T_{55} & 0 \\
-T_{61} - T_{62} - T_{63} & 0 & 0 & T_{66}\n\end{bmatrix}.
$$

In the kind *imm*2 the polar tensor in one state is

This is changed to

The axial tensor in one state is

This is changed to

In the kind i4 the polar or axial tensor in one state is

$$
\begin{bmatrix} a & b & c & 0 & 0 & f \\ b & a & c & 0 & 0 & -f \\ d & d & T_{33} & 0 & 0 & 0 \\ 0 & 0 & 0 & e & h & 0 \\ 0 & 0 & 0 & -h & e & 0 \\ g & -g & 0 & 0 & 0 & T_{66} \end{bmatrix} . (3.10)
$$

This is changed, whether polar or axial, to

where

$$
a' = a\{(\cos\beta)^4 + (\sin\beta)^4\} + b\cos\beta\sin\beta\sin2\beta
$$

+ $(f+g)\cos2\beta\sin2\beta + T_{66}(\sin2\beta)^2$,

$$
b' = a\cos\beta\sin\beta\sin2\beta + b\{(\cos\beta)^4 + (\sin\beta)^4\}
$$

- $(f+g)\cos2\beta\sin2\beta - T_{66}(\sin2\beta)^2$,

$$
f' = (a - b) \cos\beta \sin\beta \cos2\beta
$$

- $f(\cos 2\beta)^2 + g(\sin 2\beta)^2 - T_{66} \cos 2\beta \sin 2\beta$

$$
g' = (a - b) \cos\beta \sin\beta \cos2\beta + f(\sin 2\beta)^2 - g(\cos 2\beta)^2 - T_{66} \cos 2\beta \sin 2\beta,
$$

$$
T'_{66} = (a - b) \cos\beta \sin\beta \sin 2\beta
$$

$$
-(f+g)\cos 2\beta \sin 2\beta + T_{66}(\cos 2\beta)^2
$$

Therefore especially if the x axis (and hence the y axis also) is taken parallel to one of the rotation axes, the tensor (3.10) is changed to f—

In the kind i6 the polar or axial tensor in one state is

where $A = \frac{1}{2}(a-b)$. (The direction of the x axis is free.) This is changed, whether polar or axial, to
 $\begin{bmatrix} a & b & c & 0 & 0 & -f \end{bmatrix}$

In the kinds $i3R$, $i3P-I$, and $i3P-II$, the polar or axial tensor in one state is

where $A = \frac{1}{2}(a-b)$. This is changed, whether polar or axial, to f

where

$$
k' = k \cos 3\beta + m \sin 3\beta, \quad m' = k \sin 3\beta - m \cos 3\beta, l' = l \cos 3\beta + n \sin 3\beta, \quad n' = l \sin 3\beta - n \cos 3\beta.
$$

Therefore, especially if the x axis is taken parallel to one of the rotation axes,

$$
k'=k
$$
, $l'=l$, $m'=-m$, $n'=-n$;

if, instead of the x axis, the y axis is taken parallel to one of the rotation axes, then

$$
k'=-k, \quad l'=-l, \quad m'=m, \quad n'=n.
$$

4. GYROELECTRICITY AND HYPERGYROELECTRICITY IN IRREGULAR FERROELECTRICS

 $\begin{tabular}{c} & direction, of the
\n ₆₆ & ₆₇ \end{tabular} \vspace{-.05in} \begin{tabular}{c} \hline & direction, of the
\n crystal block in
\n electric direction
\n transition, and
\n in a direction per
\n may be complex
\n These awkward
\n ferroelectrics. I
\n 1ation of every$ The irregular ferroelectrics are, in general, unfit to use as gyroelectrics and hypergyroelectrics for the light propagating along a direction perpendicular to the ferroelectric direction. The orientation of the side faces, except the faces perpendicular to the ferroelectric direction, of the crystal block and the thickness of the crystal block in a direction perpendicular to the ferroelectric direction may not be unaltered by the state transition, and the components of tensorial properties in a direction perpendicular to the ferroelectric direction may be complexly changed by the state transition.

These awkward situations do not occur in the regular ferroelectrics. In the regular ferroelectrics, the orientation of every side face and the thickness in every direction are unaltered by the state transition; the gyration tensor and the component tensor ot the electrogyration tensor⁶ in the direction of the spontaneous polarization vector are, as a whole, either nonzero and reversed in sign by the state transition, nonzero and unchanged by the state transition, or invariably zero. (Which of these three cases should occur is determinate for each kind of regular ferroelectric.⁶) Thus the regular ferroelectrics are usable as gyroelectrics and hypergyroelectrics for all directions of light.

If we use the irregular ferroelectrics as gyroelectrics and hypergyroelectrics only for the light propagating along the ferroelectric direction, we see from Secs. 3.2 and 3.3 that of the eleven kinds of irregular ferroelectrics, the two kinds

(a) $i1-I$, $i2-I$

are gyroelectric, the seven kinds

(b) $i1$ -II, $i2$ -II, $i4$, $i6$, $i3R$, $i3P$ -I, $i3P$ -II

are hypergyroelectric, and the two kinds

 (c) im, imm2

are neither gyroelectric nor hypergyroelectric. When the s axis is taken parallel to the ferroelectric direction, the $(3,3)$ element G_{33} of the gyration tensor (a symmetric axial tensor of rank two) is for (a) nonzero and reversed in sign by the state transition, for (b) nonzero and unchanged by the state transition, and for (c) invariably zero; the $(3,3)$ element η_{33} of the electrogyration tensor (a partially symmetric axial tensor of rank three) is for (a) nonzero and unchanged by the state transition, for (b) nonzero and reversed in sign by the state transition, and for (c) invariably zero. Here it has been assumed for irregular hypergyroelectricity that the infinitesimal biasing electric field for measuring the electrogyration is applied in the ferroelectric direction. This corresponds to the condition on regular hypergyroelectricity⁶ that the infinitesimal biasing electric field for measuring the electrogyration be applied in the direction of the spontaneous polarization vector.

By the "irregular gyroelectrics" and the "irregular By the "irregular gyroelectrics" and the "irregular
hypergyroelectrics," we mean those stated above, i.e.,

TaBLE IV. Gyroelectricity or hypergyroelectricity of each kind of irregular ferroelectric.

Irregular	Gyroelectricity or	Irregular	Gyroelectricity or
kind	hypergyroelectricity	kind	hypergyroelectricity
$i1-I$ $i1$ -II im $i2$ -T $i2$ -II imm2	gyroelectric hypergyroelectric neither g. nor hg. gyroelectric hypergyroelectric neither g. nor hg.	i4 iб i3R $i3P-I$ $i3P$ -TT	hypergyroelectric hypergyroelectric hypergyroelectric hypergyroelectric hypergyroelectric

the irregular ferroelectrics which are, respectively, gyroelectric and hypergyroelectric for the light propagating along the ferroelectric direction. Gyroelectricity or hypergyroelectricity of each kind of irregular ferroelectric is tabulated in Table IV. Incidentally, gyroelectricity or hypergyroelectricity of each kind of regular ferroelectric is tabulated in Table V. It turns out that the irregular hypergyroelectrics are all only of rotation type and not of reflection type nor of rotatoryreflection type. This corresponds to the fact that the regular hypergyroelectrics are all only of rotation type and not of inversion type nor of reflection type.⁶

TABLE V. Gyroelectricity or hypergyroelectricity of each kind of regular ferroelectric.

Regular	Gyroelectricity or	Regular	Gyroelectricity or
kind	hypergyroelectricity	kind	hypergyroelectricity
r1 rm r2. rmm2 $r4 - I$ r4-TT r4mm r6-T r6-II r6mm	gyroelectric gyroelectric gyroelectric gyroelectric gyroelectric hypergyroelectric neither g. nor hg. gyroelectric hypergyroelectric neither g. nor hg.	$r3R$ -I $r3R$ -II r3mR $r3P$ -T $r3P-II$ $r3P-$ TTT $r3P$ -IV $r3mP$ -I $r3mP$ -II	gyroelectric hypergyroelectric neither g. nor hg. gyroelectric gyroelectric hypergyroelectric hypergyroelectric neither g. nor hg. neither g. nor hg.

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