mechanism postulated by El-Bayoumi and Kasha[70] in studies of fluorescence quenching of dimers in solution.

9. Photoconductivity

The photoconduction of aromatic crystals appears to be related to the luminescence inasmuch as those crystals which luminesce with highest efficiency are often best photoconductors. Therefore, if photoconductivity is to be efficient, the lowest excited state of the crystal should not rapidly decay nonradiatively. This, in turn, suggests that photoconductive states are not populated "vertically," but involve the relaxation of exciton waves within the Brillouin zone. A probable zone structure is shown in Fig. 12. In this representation the initial kinetic energy of an exciton $[\epsilon(0) - \epsilon(\mathbf{k})]$ is larger than the binding energy $\epsilon(d)$ of the exciton, which is then able to dissociate into a free electron and a hole by emitting or absorbing phonons. In this example exciton absorption contributes directly to the photoconductivity which would necessitate that the photoelectric threshold and the exciton origin be reasonably close together. Such is apparently not the case for molecular crystals where there can be a gap of up to 2 to 3 eV. The presence of defects or impurities could provide other pathways for exciton dissociation if there were sufficient energy available at the active sites. Conjectures of this nature could readily be tested experimentally, by measurements of reflexion spectra, quantum yields, excitation spectra of slow fluorescence, photoconductive anisotropy, and the slow fluorescence of crystals in strong electric fields.

ACKNOWLEDGMENTS

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[70] M. Ashraf El-Bayoumi and M. Kasha, J. Chem. Phys. **34**, 3181 (1961).

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Polarization, Pyroelectricity, and Ferroelectricity of Ionic Crystals

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CONTENTS

1. INTRODUCTION

THE polarization of the dielectric crystal has been defined as, or conceived as being equal to, the electric dipole moment of the unit cell divided by the volume of the unit cell; analogous to the magnetization of the magnetic crystal. Such a definition or conception has not particularly been felt awkward, until the discovery and investigation of many ferroelectric and pyroelectric crystals in recent years. These crystals are mostly of poor symmetry and of ionic character, and are conceived to be characterized by "spontaneous polarization" (polarization at zero electric field). In poorly symmetrical crystals, there is a fair arbitrariness in selecting their unit cell. In the crystals of ionic character, it is easily seen that the dipole moment of unit cell may vary with the type of unit cell selected. Therefore, especially for ferroelectric and pyroelectric crystals, the conventional concept of polarization proves more or less obscure. This leads to the obscurity of other dielectric concepts, since they are based on the concept of polarization.

In this paper, we attempt to make clear and exact the concepts of polarization and other dielectric characteristics of the ionic crystals general. We first consider polarization; then, the new concepts of "boundary polarization," "reference structure," and "orderly and stationary reference structure" have to be introduced. "Reference structure" is to be employed in place of "unit cell;" the former is more suitable for our general argument. On the basis of this consideration, we next discuss pyroelectric coefficient and susceptibility, and finally, investigate pyroelectricity, ferroelectricity, and spontaneous polarization.

In this paper, we are not concerned with the problem of the origin of ferroelectricity or pyroelectricity, or more generally, the problem of why a particular crystal has such a structure.

2. POLARIZATION

2.1. A Theorem of Electrostatics and the Meaning of Polarization

There is a well-known theorem of electrostatics to be presented at the outset. We suppose two infinite plane electrodes separated by a distance l and both grounded. Then, the theorem is that if a point charge q is located between the electrodes at a distance u from one of them, the charge induced on that electrode is $-q(1 - u/l)$. From this theorem it follows that a dipole (not necessarily a *point* dipole) $\mathbf{p}$ between the electrodes induces a charge $\mathbf{p}\cdot\mathbf{n}/l$ on the negative-side electrode (referring to the common normal-vector $\mathbf{n}$ of the electrodes). It is noted that the induced charge depends on the position of the point charge but not on that of the dipole. The diameters of the electrodes have been assumed to be infinite, but, in practice, they have merely to be large enough compared with l.

We consider the meaning of "polarization." For this purpose, it is supposed that a macroscopically homogeneous crystal plate of a thickness l is in contact with two electrodes; the diameter of the crystal plate is large enough compared with l, and the electrodes cover the main faces of the crystal plate entirely. The areas of the crystal plate and electrodes are denoted by S and S', respectively. In this paper, the normal component of the "polarization vector" of the crystal plate is referred to briefly as the "polarization" of the crystal plate. If the polarization of the crystal plate is P, and the potential difference between the electrodes is V, and the charge on the negative-side electrode is Q, then the relation

$$Q = SP + S'V/4\pi l$$

holds in practice. P is actually dependent on V, but for the validity of the above relation such dependence is not necessary, and it can be conceived that P and V cause Q independently of one another. Even though the potential difference varies, the polarization is the same if the configuration of the charges composing the crystal plate remains as it is. Therefore, the polarization P of the crystal plate at a certain potential difference V can be interpreted as $P = Q_0/S$, where Q_0 is the charge which would accumulate on the electrode if the potential difference were brought from V to zero without modifying the charge configuration of the crystal plate. The polarization can yet be reinterpreted, as follows. The polarization of the crystal plate at a certain potential difference is equal to the charge which would be induced on the negative-side electrode by the substance within a cylinder running through the crystal plate, with its bottom of unit area, if both electrodes were to be grounded without modifying the charge configuration. It is advantageous to interpret the polarization in this form; for, the polarization can then be calculated from the knowledge of the configuration of the charges composing the crystal plate, with the help of the previous theorem of electrostatics.

2.2. Crystals to be Treated

In this paper, we are concerned with the crystals of ionic character. They will be referred to simply as crystals. It is assumed that they have neither electronic, nor ionic, electrical conductivity. We often imagine an infinite crystal that has no boundaries. The *crystal plates*, of a crystal (species), having various Miller indices and various boundaries can be imagined to have been cut out from its infinite crystal; their internal structures are conceived to be identical with each other and to be definite at a given temperature, a given electric field, and a given strain or stress. Temperature, electric field, strain, and stress in this paper are of a macroscopic concept and uniform over the whole crystal or the whole crystal plate. A crystal to be treated can have disorder (as potassium dihydrogen phosphate and sodium nitrite). For convenience of consideration, each of the ions (or atoms) composing a crystal is replaced by a point charge and a point dipole located at its nucleus. This simplification is adequate for the essence of our argument.

2.3. Connection between Polarization and Configuration Parameters

A crystal structure is represented by a reference space lattice and a basis. When two space lattices can be superimposed by a parallel displacement, they are provisionally referred to as parallel to one another. Any space lattice parallel to a certain reference space lattice can be adopted as another reference space lattice. The three fundamental translation vectors of a given crystal are denoted by $\mathbf{a}$, $\mathbf{b}$, and $\mathbf{c}$. The volume per lattice point is denoted by v. All the ions composing the basis are numbered. In case the crystal has disorder, all the positions the ith ion can occupy are numbered. The jth position of the ith ion is briefly designated as the (i,j) position. The vector getting from the point of the reference space lattice to the (i,j) position in the same basis is denoted by $\mathbf{s}_{ij}$. The charge and dipole of the ith ion at the (i,j) position are denoted by q_{ij} and $\mathbf{p}_{ij}$, respectively. The probability that the ith ion occupies the (i,j) position is denoted by f_{ij}. (It is unessential whether the positions occupied by the ith ion are discrete or continuous; we assume that they are discrete.) It is obvious that

$$\sum_j f_{ij} = 1\,. \tag{2.1}$$

As the requirement for electrical neutrality of the crystal, the equation

$$\sum_{i,j} f_{ij} q_{ij} = 0 \tag{2.2}$$

must be satisfied.

We connect the polarization of the crystal plate with the charge-configuration parameters of the crystal. The crystal plate has the indices $(h_1h_2h_3)$, the normal vector $\mathbf{n}$, and the thickness l; its diameter is large enough compared with l. For the present, we set the following assumption, which will later be revised. The surface parts of the crystal plate include no vacancies, and the configuration parameters $\mathbf{s}_{ij}$, q_{ij}, etc., are uniform over the central and surface parts of the crystal plate. We imagine the crystal plate within the infinite crystal. In order to carry out the calculation according to Sec. 2.1, we imagine two grounded electrodes in contact with the crystal plate. Out of the $(h_1h_2h_3)$ planes of the reference space lattice, one is arbitrarily chosen as the $(h_1h_2h_3)$ *datum plane*. The distance of that plane from the negative-side electrode (referring to $\mathbf{n}$) is denoted by l_0. A plane which is parallel to an $(h_1h_2h_3)$ lattice plane and goes through (i,j) positions is briefly designated as an (i,j)-$(h_1h_2h_3)$ plane. The (i,j)-$(h_1h_2h_3)$ plane which is distant by $\mathbf{n}\cdot\mathbf{s}_{ij}$ from the $(h_1h_2h_3)$ datum plane is referred to as the (i,j)-$(h_1h_2h_3)$ datum plane. When the spacing between two adjoining $(h_1h_2h_3)$ lattice planes is denoted by d, an arbitrary (i,j)-$(h_1h_2h_3)$ plane is distant from the (i,j)-$(h_1h_2h_3)$ datum plane by $n_{ij}d$ (n_{ij}: an integer), and hence from the negative-side electrode by $l_0 + \mathbf{n}\cdot\mathbf{s}_{ij} + n_{ij}d$. The total number of the (i,j)-$(h_1h_2h_3)$ planes between the electrodes is denoted by N_{ij}. An (i,j)-$(h_1h_2h_3)$ plane contains $f_{ij}d/v$ ith ions per unit area; hence, for electrical neutrality of the crystal plate, the equation

$$\sum_{i,j}\sum_{n_{ij}=k_{ij}}^{k_{ij}+N_{ij}-1}\frac{f_{ij}d}{v}q_{ij}=0$$

or

$$\textstyle\sum_{i,j} N_{ij}f_{ij}q_{ij} = 0 \tag{2.3}$$

must be satisfied, where k_{ij} is the n_{ij} of that (i,j)-$(h_1h_2h_3)$ plane which is the nearest to the negative-side electrode.

The polarization P of the crystal plate is calculated as follows:

$$\begin{aligned}P &= \sum_{i,j}\sum_{n_{ij}=k_{ij}}^{k_{ij}+N_{ij}-1}\frac{f_{ij}d}{v}\\ &\quad\times\left\{-q_{ij}\left(1-\frac{l_0+\mathbf{n}\cdot\mathbf{s}_{ij}+n_{ij}d}{l}\right)+\frac{\mathbf{n}\cdot\mathbf{p}_{ij}}{l}\right\}\\ &= \frac{d}{vl}\sum_{i,j}N_{ij}f_{ij}q_{ij}(\mathbf{n}\cdot\mathbf{s}_{ij}+k_{ij}d+\tfrac{1}{2}N_{ij}d)\\ &\quad+\mathbf{n}\cdot\frac{d}{vl}\sum_{i,j}N_{ij}f_{ij}\mathbf{p}_{ij}\,.\end{aligned}$$

Now, we set the second $(h_1h_2h_3)$ datum plane, to which an $(h_1h_2h_3)$ lattice plane is selected. The (i,j)-$(h_1h_2h_3)$ plane distant by $\mathbf{n}\cdot\mathbf{s}_{ij}$ from that plane is the second (i,j)-$(h_1h_2h_3)$ datum plane. If the second $(h_1h_2h_3)$ datum plane is distant from the first one by kd, and the (i,j)-$(h_1h_2h_3)$ plane nearest to the positive-side electrode is distant from the second (i,j)-$(h_1h_2h_3)$ datum plane by $k'_{ij}d$, then

$$k_{ij} + N_{ij} - 1 = k + k'_{ij}\,. \tag{2.4}$$

The number of the (i,j)-$(h_1h_2h_3)$ planes N_{ij} might not be independent of i, but there is a number N such that $|N_{ij} - N| \leqslant 1$ (or 2 or the like) over all i and j. Employing k'_{ij} and N, we have

$$\begin{aligned}P &= \frac{Nd}{vl}\sum_{i,j}f_{ij}q_{ij}\left(\mathbf{n}\cdot\mathbf{s}_{ij}+\frac{k_{ij}+k'_{ij}}{2}d\right)\\ &\quad+\mathbf{n}\cdot\frac{Nd}{vl}\sum_{i,j}f_{ij}\mathbf{p}_{ij}\\ &\quad+\frac{d}{vl}\sum_{i,j}(N_{ij}-N)f_{ij}q_{ij}\left(\mathbf{n}\cdot\mathbf{s}_{ij}+\frac{k_{ij}+k_{ij}'}{2}d\right)\\ &\quad+\mathbf{n}\cdot\frac{d}{vl}\sum_{i,j}(N_{ij}-N)f_{ij}\mathbf{p}_{ij}\,.\end{aligned}$$

The last two terms on the right-hand side can be neglected since they are, ordinarily, far smaller than the first two terms. [It is noted, from (2.2) and (2.3), that $\sum_{i,j}(N_{ij} - N)f_{ij}q_{ij} = 0$.] It is obvious that $Nd \approx l$. Thus, we get to

$$\begin{aligned}P &\approx \mathbf{n}\cdot\frac{1}{v}\left\{\sum_{i,j}f_{ij}q_{ij}(\mathbf{s}_{ij}-\mathbf{g}_{ij})+\sum_{i,j}f_{ij}\mathbf{p}_{ij}\right\}\\ &\quad+\frac{1}{v}\left\{\sum_{i,j}f_{ij}q_{ij}\left(\frac{k_{ij}+k'_{ij}}{2}\right)d\right.\\ &\quad\left.+\sum_{i,j}f_{ij}q_{ij}(\mathbf{n}\cdot\mathbf{g}_{ij})\right\},\end{aligned} \tag{2.5}$$

where $\mathbf{g}_{ij}$ are certain vectors. If we put

$$\mathbf{P}_v = (1/v)\,\{\textstyle\sum_{i,j} f_{ij}q_{ij}(\mathbf{s}_{ij} - \mathbf{g}_{ij}) + \sum_{i,j} \jmath_{ij}\mathbf{p}_{ij}\} \tag{2.6}$$

and

$$\begin{aligned}P_f &= \frac{1}{v}\left\{\sum_{i,j}f_{ij}q_{ij}\left(\frac{k_{ij}+k'_{ij}}{2}\right)d\right.\\ &\quad\left.+\sum_{i,j}f_{ij}q_{ij}(\mathbf{n}\cdot\mathbf{g}_{ij})\right\},\end{aligned} \tag{2.7}$$

then (2.5) becomes

$$P = \mathbf{n}\cdot\mathbf{P}_v + P_f\,. \tag{2.8}$$

(Here, $=$ has been employed instead of $\approx$. It is immaterial which is employed.)

It is seen that P consists of both P_f and the normal component of $\mathbf{P}_v$. Equations (2.6), (2.7), and (2.8) give the connection between the polarization and the configuration parameters. The quantities $\mathbf{P}_v$, $\mathbf{n}\cdot\mathbf{P}_v$, and P_f are provisionally referred to as the "bulk polarization vector" (briefly, bk.p.v.), "bulk polarization" (briefly, bk.p.), and "boundary polarization" (briefly, bd.p.), respectively.

2.4. Reference Structure, Bulk Polarization Vector, and Boundary Polarization

The position vectors $\mathbf{s}_{ij}$ give the structure of the crystal; likewise, the position vectors $\mathbf{g}_{ij}$ give some kind of structure, which is temporarily referred to as the "proto-structure." Many different $\mathbf{s}$ sets can represent the same crystal structure. (The $\mathbf{s}$ set is the set which consists of the vectors $\mathbf{s}_{ij}$.) Similarly, various $\mathbf{g}$ sets are conceivable which represent the same proto-structure. As seen from (2.6), the bk.p.v. is to be determined by comparing the crystal structure with the proto-structure. For this comparison, the specification only of each of these structures is not sufficient; we must yet specify the *connection* between them, that is, which one of the (i,j) positions in the proto-structure corresponds to an arbitrary one of the (i,j) positions in the crystal structure. (The (i,j) positions, by themselves, form a space lattice.) Therefore, it is convenient to employ the concept which involves the "connection" in addition to the "proto-structure"; this is provisionally referred to as the "reference structure" (briefly, r.s.). If the set of $\mathbf{s}_{ij}$ and $\mathbf{g}_{ij}$ and the set of $\mathbf{s}^*_{ij}$ and $\mathbf{g}^*_{ij}$ are representative of the same crystal structure and the same r.s., then it is conceived that $\mathbf{s}^*_{ij} - \mathbf{g}^*_{ij} = \mathbf{s}_{ij} - \mathbf{g}_{ij}$, or more generally $\mathbf{s}^*_{ij} - \mathbf{g}^*_{ij} = \mathbf{s}_{ij} - \mathbf{g}_{ij} + \mathbf{A}$ ($\mathbf{A}$: a certain vector), over all i and j. If the **s** set is reselected otherwise, the **g** set must also be done in order to represent the same r.s. A reference structure often corresponds to a type of unit cell. For the general consideration of polarization, etc., of ionic crystals, the concept of "reference structure" is more expedient than that of "unit cell." In this paper, therefore, the former is generally employed in place of the latter.

The bk.p.v. is determined by specifying the r.s., but is independent of the particular representations of the r.s. The bk.p.v. has no connection with the boundaries of the crystal plate. The polarization is dependent upon the boundaries, but independent of the r.s. The bd.p. depends on the boundaries. It depends, further, on the r.s., but not on the particular representations of the r.s.

In order to make the newly introduced concepts clearer, we consider a model crystal, which is shown in Fig. 1. The crystal consists of two kinds of ions and has no disorder. The first and the second ions possess a positive charge q and a negative charge $-q$, respectively, and have no dipoles. The fundamental translation vectors **a** and **b** are parallel to the paper face, and **c** is normal to that. Full circles and open ones are projections of first- and second-ion positions, respectively. Points A,B,C,D, and E are positive-ion positions in a plane parallel to the paper face. At a distance **c** from them, there are points A′,B′,C′,D′, and E′, respectively. Point F is a negative-ion position between the planes ABC and A′B′C′. Points G and H are the body centers of the hexahedrons ABCDA′B′C′D′ and ABCEA′B′C′E′, respectively. In this crystal, Eq. (2.6) becomes

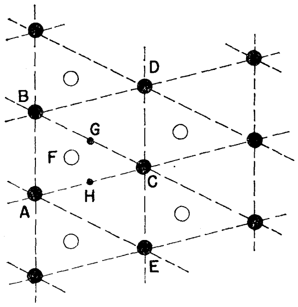

FIG. 1. Model crystal. Fundamental translation vectors **a** and **b** are parallel to the paper face, and **c** is normal to that. Full circles and open ones are projections of positions of positive first ions and negative second ions, respectively.

$$\mathbf{P}_v = (q/v)\{(\mathbf{s}_1 - \mathbf{g}_1) - (\mathbf{s}_2 - \mathbf{g}_2)\}\ .$$

(i) If we set $\mathbf{s}_1 = 0$, $\mathbf{s}_2 = \overrightarrow{\mathrm{AF}}$, $\mathbf{g}_1 = 0$, and $\mathbf{g}_2 = \overrightarrow{\mathrm{AG}}$, then $\mathbf{s}_1 - \mathbf{g}_1 = 0$, $\mathbf{s}_2 - \mathbf{g}_2 = \overrightarrow{\mathrm{GF}}$, and $\mathbf{P}_v = (q/v)\overrightarrow{\mathrm{FG}}$;

(ii) if we set $\mathbf{s}_1 = 0$, $\mathbf{s}_2 = \overrightarrow{\mathrm{CF}}$, $\mathbf{g}_1 = 0$, and $\mathbf{g}_2 = \overrightarrow{\mathrm{CG}}$, then $\mathbf{s}_1 - \mathbf{g}_1 = 0$, $\mathbf{s}_2 - \mathbf{g}_2 = \overrightarrow{\mathrm{GF}}$, and $\mathbf{P}_v = (q/v)\overrightarrow{\mathrm{FG}}$;

(iii) if we set $\mathbf{s}_1 = 0$, $\mathbf{s}_2 = \overrightarrow{\mathrm{AF}}$, $\mathbf{g}_1 = 0$, and $\mathbf{g}_2 = \overrightarrow{\mathrm{AH}}$, then $\mathbf{s}_1 - \mathbf{g}_1 = 0$, $\mathbf{s}_2 - \mathbf{g}_2 = \overrightarrow{\mathrm{HF}}$, and $\mathbf{P}_v = (q/v)\overrightarrow{\mathrm{FH}}$;

(iv) if we set $\mathbf{s}_1 = \overrightarrow{\mathrm{HA}}$, $\mathbf{s}_2 = \overrightarrow{\mathrm{HF}}$, $\mathbf{g}_1 = 0$, and $\mathbf{g}_2 = \overrightarrow{\mathrm{HC}}$, then $\mathbf{s}_1 - \mathbf{g}_1 = \overrightarrow{\mathrm{HA}}$, $\mathbf{s}_2 - \mathbf{g}_2 = \overrightarrow{\mathrm{HF}} + \overrightarrow{\mathrm{HA}}$, and $\mathbf{P}_v = (q/v)\overrightarrow{\mathrm{FH}}$.

The r.s. in (i) is the same as that in (ii), and the r.s. in (iii) is the same as that in (iv), but the r.s. in (i) differs from that in (iii). The r.s. in (i) corresponds to the type of unit cell that consists of one negative ion existing at F and one positive ion existing, in the form of eight identical parts, at A,B,C,D,A′,B′,C′, and D′. The type of unit cell corresponding to the r.s. in (iii) consists of one negative ion existing at F and one positive ion existing, in the form of eight identical parts, at A,B,C,E,A′,B′,C′, and E′.

The concept of bd.p. is new. Polarization has often been conceived equal to what corresponds to our bk.p.; this conception is valid in case bd.p. is negligibly small compared with bk.p.; but in other cases it is not valid. As to a given crystal plate, its polarization is unique, but its bk.p. and bd.p. are not so. We remember that they are dependent upon the particular r.s. selected.

2.5. Illustration of Bulk Polarization and Boundary Polarization

The model crystal shown in Fig. 2. will serve for the illustration of bk.p. and bd.p. It consists of two kinds of ions and has no disorder. The first and the second ion possess a negative charge $-q$ and a positive charge q, respectively, and have no dipoles. The fundamental translation vector **a** is normal to the paper face, **c** is parallel to that and orients from left to right horizontally, and **b** is normal to the former two. Open circles and full ones are projections of first- and second-ion positions, respectively. Points A,B,C, and D are negative-ion positions in a plane parallel to the paper face. At a distance **a** from them, there are points A′,B′,C′, and D′, respectively. Point F is the body center of the hexahedron ABCD-A′B′C′D′; G is the face center of the rectangle

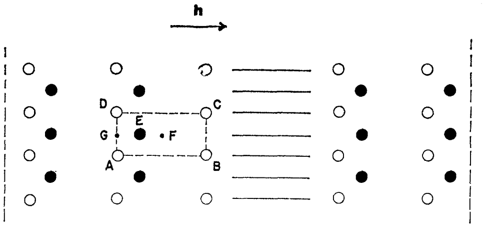

FIG. 2. Model crystal plate. The fundamental translation vector **a** is normal to the paper face, **c** is parallel to that and horizontal, and **b** is normal to the former two. Open circles and full ones are projections of positions of negative first ions and positive second ions, respectively.

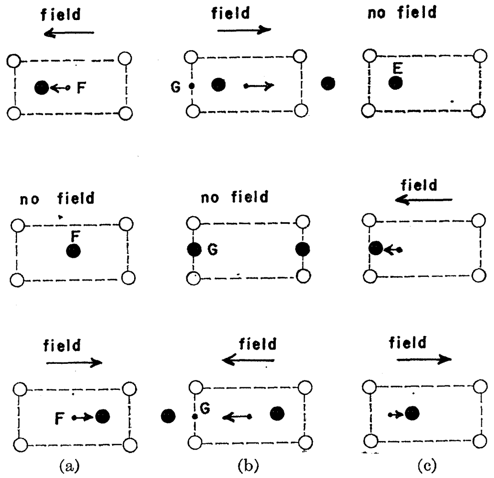

FIG. 3. Three different cases for the displacement of ions by electric field. In the uppermost three, the ionic configurations are the same, but the applied electric fields are different.

ADA′D′; E is a positive-ion position on the line segment FG; we put $\overline{\mathrm{EF}} = u$ and $\overline{\mathrm{EG}} = w$. The normal vector **n** of the crystal plate is parallel to **c**. We put

$$\mathbf{s}_1 = 0, \quad \mathbf{s}_2 = \mathbf{s}, \quad \mathbf{g}_1 = 0, \quad \text{and} \quad \mathbf{g}_2 = \mathbf{g}\ ;$$

then,

$$P_v = \mathbf{n}\cdot\mathbf{P}_v = (q/v)\mathbf{n}\cdot(\mathbf{s}-\mathbf{g})$$

and

$$P_f = (qc/2v)\{(k_2 - k_1) + (k_2' - k_1')\} + (q/v)\mathbf{n}\cdot\mathbf{g}\ .$$

If we set $\mathbf{s} = \overrightarrow{\mathrm{AE}}$, then

$$k_1 = k_2,\ k_1' = k_2', \text{ and } P_f = (q/v)\mathbf{n}\cdot\mathbf{g}\ ;$$

if we set $\mathbf{s} = \overrightarrow{\mathrm{BE}}$, then

$$k_2 - k_1 = k_2' - k_1' = 1 \text{ and } P_f = (q/v)c + (q/v)\mathbf{n}\cdot\mathbf{g}\ .$$

Various r.s.'s are conceivable, but only three typical ones will be taken up. We set $\mathbf{s} = \overrightarrow{\mathrm{AE}}$, provisionally.

Reference Structure I. We select

$$\mathbf{g} = \overrightarrow{\mathrm{AF}} \quad \text{and} \quad \mathbf{s} - \mathbf{g} = \overrightarrow{\mathrm{FE}}\ .$$

This r.s. corresponds to the type of unit cell that consists of one positive ion existing at E and one negative ion existing, in parts, at the eight points A,B,C,D,A′,B′,C′, and D′. This r.s. may be adopted in case the positive ion, as shown in Fig. 3(a), is mobile in the sense of electric field about F as center. In the present instance,

$$P_v = -(qu/v), \quad P_f = qc/2v, \quad P = qw/v\ .$$

The bk.p. is negative; therefore, viewing the unit cell alone, the crystal plate appears as if it were polarized in the negative sense. The fact is, however, that the crystal plate is polarized in the positive sense. The contribution of P_f to P overcomes that of P_v.

Reference Structure II. We select

$$\mathbf{g} = \overrightarrow{\mathrm{AG}} \quad \text{and} \quad \mathbf{s} - \mathbf{g} = \overrightarrow{\mathrm{GE}}\ .$$

This r.s. corresponds to the type of unit cell that consists of one positive and one negative ion, the former existing, in the form of two identical parts, at both E and the point distant by **c** from E, and the latter existing, in the form of eight identical parts, at A,B,C,D,A′,B′,C′, and D′. This r.s. may be adopted in case the positive ion, as shown in Fig. 3(b), is mobile in the sense of electric field about G as center. In the present instance,

$$P_v = qw/v, \quad P_f = 0, \quad P = P_v = qw/v\ .$$

Since the bd.p. is zero, the polarization is equal to the bk.p. The bk.p. and the bd.p. in R.S. I are not equal to those in R.S. II, respectively, but the polarization is, of course, equal in both r.s.'s.

Reference Structure III. We select

$$\mathbf{g} = \overrightarrow{\mathrm{AE}} \quad \text{and} \quad \mathbf{s} - \mathbf{g} = 0\ .$$

The type of unit cell corresponding to this r.s. is not simple. This r.s. might be advantageous in case the positive ion, as shown in Fig. 3(c), is mobile in the sense of electric field about E as center. Now,

$$P_v = 0, \quad P_f = qw/v, \quad P = P_f = qw/v\ .$$

It is seen that P consists of P_f alone.

We can also set $\mathbf{s} = \overrightarrow{\mathrm{BE}}$. Then, in order to represent, for instance, R.S. I, we have merely to select $\mathbf{g} = \overrightarrow{\mathrm{BF}}$.

2.6. Boundary Polarization Involving Surface Effect

So far, we have been assuming that the surface parts of the crystal plate include no vacancies. If we adhere to this assumption, we shall deviate far from reality. We consider, for example, the (001) crystal plate of cesium chloride. Both its extremities would then be a perfect plane of chloride ions on one side, and a perfect plane of cesium ions on the other side. (Then, the crystal plate is electrically neutral.) The crystal plate would therefore have a large polarization at null field. This is not the case, however. As is known, opposite senses of the normal of the (001) crystal plate of cesium chloride are equivalent (in symmetry) to one another; in an ordinary sample of the crystal plate (species), therefore, its surface parts on opposite sides are expected to be almost identical. In order to express such identity in our treatment, we have to take into consideration vacancies in the surface parts. This is also consistent with the fact that any real crystal plate of best quality includes thermally-caused vacancies in its surface parts. (Vacancies in the central part are, usually, very sparse.) We have also been assuming that the configuration parameters are uniform over the central and surface parts of the crystal plate. Is this too simple?

It is proper that the above-mentioned surface effect is involved in bd.p. We denote this correction term by ΔP_f. The density of vacancies can be represented in terms of f_{ij}, though the former concept is, originally, different from the latter; in this case Eq. (2.1) does not hold. It is assumed that the thickness of each surface part is far smaller than the total thickness of the crystal plate. Now, we estimate the degrees of contribution to ΔP_f of the variations in the configuration parameters within the surface parts. For this purpose, we consider a one-dimensional model crystal, which consists of positive and negative ions alternating. (The crystal plate is one-dimensional in treatment.) In the central part, the charges of the positive and the negative ion are q and $-q$, respectively, and the interval between two adjoining positive and negative ions is c. The thickness (or length) of the crystal is l. At first, the crystal ends with a negative and a positive ion on the left- and the right-hand side, respectively, and the ionic charges and the interval between ions are uniform over the central and surface parts.

The dipole moment of a pair of adjoining positive and negative ions is qc at first, but it varies by qc if the interval becomes $2c$, and by $qc/2$ if $c/2$. Therefore, the contribution to ΔP_f of the variations in the lattice constants or the position vectors $\mathbf{s}_{ij}$ within the surface parts is thought to be of the order of Aqc (A : a certain coefficient). The case, in the crystal plate, that vacancies are present in the surface parts corresponds to the case, in the linear model crystal, that the crystal ends with fractional ions. It is now supposed that the negative ion at the left-hand extremity is bisected and one half is left there and the other half is brought to the right-hand extremity; or that a half negative ion is added to the right-hand extremity and a half positive ion is superimposed on the negative ion at the left-hand extremity. By this operation, both extremities become identical. This operation varies the dipole moment of the whole linear crystal by $ql/2$. Therefore, the contribution to ΔP_f of the vacancies within the surface parts may be of the order of Aql. The contribution to ΔP_f of the variations in the charges q_{ij} within the surface parts is considered to be of the order of Aqc. For, if the charges of two adjoining positive and negative ions become doubled, the dipole moment varies by qc; and if halved, then the moment varies by $qc/2$. A conception might here occur: If only the charges of the negative and the positive ion at the extremities were to vary, the contribution of the variations in the ionic charges would be of the same order as that of the vacancies. This contribution is, however, to be regarded as of the space charges due to conductive electrons. We remember that, in this paper, we are concerned with the nonconductive crystals. This case is therefore excluded. It may be reasonable to estimate the contribution of the variations in the dipole moments $\mathbf{p}_{ij}$ as being of the same order as that of the variations in the charges q_{ij}.

From the above consideration, it is evident that the vacancy effect is prominent. Hence, it may be reasonable to assume that the surface effect is represented by the vacancy effect alone, the other contributions being left out of consideration. There are other thermally-caused imperfections that have not been considered above; their effects may also be negligibly weak compared with the vacancy effect.

We calculate the correction term ΔP_f due to the vacancy effect. The number of ith ions per area v/d, in the kth (i,j)-$(h_1h_2h_3)$ plane, in the negative- (or positive-) side surface part is denoted by f_{ijk} (or f'_{ijk}). As the requirement for electrical neutrality, the equation

$$\sum_{i,j,k} \frac{d}{v}(f_{ijk} - f_{ij})q_{ij} + \sum_{i,j,k} \frac{d}{v}(f'_{ijk} - f_{ij})q_{ij} = 0$$

must be satisfied. It may be obvious that

$$\Delta P_f = -\sum_{i,j,k} \frac{d}{v}(f_{ijk} - f_{ij})q_{ij} .$$

If we put

$$\theta_{ijk} = (f_{ij} - f_{ijk})/f_{ij} \quad \text{or} \quad f_{ijk} = f_{ij}(1 - \theta_{ijk}) , \quad (2.9)$$

then

$$\Delta P_f = \frac{1}{v} \sum_{i,j,k} \theta_{ijk} f_{ij} q_{ij} d \, .$$

Thus, we have

$$P_f = \frac{1}{v} \left\{ \sum_{i,j} f_{ij} q_{ij} \left(\frac{k_{ij} + k'_{ij}}{2} \right) d + \sum_{i,j} f_{ij} q_{ij} (\mathbf{n} \cdot \mathbf{g}_{ij}) + \sum_{i,j,k} \theta_{ijk} f_{ij} q_{ij} d \right\}, \quad (2.10)$$

as the new bd.p.

For the illustration of the new third term, we consider the model crystal shown in Fig. 2. The crystal is now a little modified: There are vacancies in the surface parts, the elements of the θ set being θ_{11}, θ_{21}, θ_{12}, θ_{22}, etc., from the left-hand extremity successively (the subscript j is unnecessary since this crystal has no disorder). The third term is

$$(qc/v)(-\theta_{11} + \theta_{21} - \theta_{12} + \theta_{22} - \cdots) \, .$$

If R.S. I (see Sec. 2.5) is selected,

$$P_f = (qc/v)(1/2 - \theta_{11} + \theta_{21} - \theta_{12} + \theta_{22} - \cdots) \, .$$

Hence, provided that

$$\theta_{11} - \theta_{21} + \theta_{12} - \theta_{22} + \cdots = 1/2$$

then

$$P_f = 0 \quad \text{and} \quad P = P_v = -\, qu/v \, .$$

We note that, in this case, the polarization is equal to the bk.p.

If R.S. III is selected,

$$P_f = (qc/v)(w/c - \theta_{11} + \theta_{21} - \theta_{12} + \theta_{22} - \cdots) \, .$$

Hence, provided that

$$\theta_{11} - \theta_{21} + \theta_{12} - \theta_{22} + \cdots = w/c \, ,$$

then

$$P_f = 0, \quad P_v = 0, \quad P = 0 \, ;$$

as the bk.p. is zero, so the polarization is zero.

As above illustrated, if *ordinary* samples of a crystal plate (species) have unique boundaries (or surfaces) in a pair, the crystal plate (species) has a r.s. that gives *ordinarily* $P_f \approx 0$. (This problem will again be considered in Sec. 4.4.)

2.7. Treatment of Group Ions

A group ion, such as a nitrite ion, always behaves as one group. Each of the atoms (or ions) composing a group ion can be regarded as a carrier of a point charge and a point dipole; but it is more advantageous to replace the whole group ion by a point charge and a point dipole; for, it is then unnecessary to know the effective charges and dipoles of the constituent atoms (or ions). One way of the replacement is as follows. We take the nitrite ion as an example. This group ion, as a whole, possesses a charge of -1 (electron) unit. Now, it is supposed that two point charges, 1 unit and -1 unit, are put on the nitrogen nucleus. One of them, 1 unit, forms a dipole $\mathbf{p}$ in combination with the charge -1 unit originally present within the group ion. This dipole can be replaced by the *point* dipole of the same moment. There are three nuclei in the nitrite ion; it is immaterial at which of them this point dipole is located, but we locate it at the nitrogen nucleus. The nitrite ion has thus been replaced by a point charge -1 unit and a point dipole $\mathbf{p}$ both situated at the nitrogen nucleus. The oxygen atoms are *veiled* by this replacement. The two point charges, 1 unit and -1 unit, can also be put on one of the oxygen nuclei instead of the nitrogen nucleus. Then, the nitrite ion is replaced by a point charge -1 unit and a point dipole $\mathbf{p}'$ ($\neq \mathbf{p}$) both situated at that oxygen nucleus. The other oxygen atom and the nitrogen atom are veiled by this replacement. It can happen that there is disorder about the position, orientation, or substance of a group ion in a crystal; if so, an f set is employed as in monatomic ions.

2.8. Orderly Reference Structure

In a disordered crystal, the number of the positions the ith ion can occupy may be more than one; the (i,j) positions, by themselves, form a space lattice, which is temporarily referred to as the (i,j) space lattice. One ith ion existing at a point, say, "A", of the (i,j') space lattice will soon move to a point of the (i,j'') space lattice. In an ordinary crystal, this new point may be uniquely determinate—we call the point "B"—and, conversely, one ith ion existing at B may move to A whenever it moves to a point of the (i,j') space lattice. This may be the case with all i and j. In such a crystal, there is an $\mathbf{s}$ set that makes *k_{ij},k'_{ij}, and $\sum_k \theta_{ijk}$ quite, or almost, independent of j*, or

$$k_{ij} = k_i, \quad k'_{ij} = k'_i, \quad \sum\nolimits_k \theta_{ijk} \approx \Theta_i \, , \quad (2.11)$$

for an *arbitrary* sample of a crystal plate (species), with *arbitrary* indices, of the crystal, at a given temperature and null field. (For instance, $\mathbf{s}_{ij}' = \overline{\mathrm{OA}}$, $\mathbf{s}_{ij}'' = \overline{\mathrm{OB}}$, etc., where O is a point of the reference space lattice.) This $\mathbf{s}$ set is provisionally referred to as "orderly." If, further, $\mathbf{g}_{ij}$ are selected so that they are independent of j or $\mathbf{g}_{ij} = \mathbf{g}_i$, the set of $\mathbf{s}_{ij}$ and $\mathbf{g}_{ij}$ is referred to as orderly. The r.s. which can be represented by an orderly $\mathbf{s}$-$\mathbf{g}$ set is referred to as orderly. (The orderly r.s. can also be represented by a nonorderly **s-g** set.) The concept of "orderly r.s." is useful; for, the bk.p.v. and the bd.p. have no direct connection with the particular representations of the r.s. It is obvious that "orderliness" does not concern the crystals without disorder, or that any **s-g** set or any r.s. is orderly in these crystals. Which **s-g** set or which r.s. is orderly can, usually, be presumed from the investigation of the crystal structure. If we select an orderly **s-g** set, Eq. (2.10) becomes

$$P_f \approx \frac{1}{v}\left\{\sum_i q_i\left(\frac{k_i+k_i'}{2}\right)d + \sum_i q_i(\mathbf{n}\cdot\mathbf{g}_i) + \sum_i \Theta_i q_i d\right\}, \tag{2.12}$$

where

$$\textstyle\sum_j f_{ij}q_{ij} = q_i\,. \tag{2.13}$$

There might be a crystal as follows: When an *i*th ion existing at A, a point of the (i,j') space lattice, is to move to a point of the (i,j'') space lattice, the new point is indeterminate, or in other words, the probabilities of its moving to a point B and another point B′ are equal to one another. Such a crystal is not expected to have any orderly **s** set; it would exhibit some anomalies. In this paper, every crystal treated is assumed to have orderly **s** sets.

3. PYROELECTRIC COEFFICIENT AND SUSCEPTIBILITY AT CONSTANT STRAIN

3.1. Stationary Reference Structure

The arguments of polarization difference, pyroelectric coefficient, and susceptibility at *constant strain* are considerably different from those at *null stress*. In this section, we consider these arguments at constant strain, and in the next section at null stress. It is to be noted that "strain" in this paper is that in thermodynamics. (Hence, thermal expansion at null stress leads to variation in strain.)

It is convenient to employ the concept of "stationary" r.s. We denote by $\Delta\mathbf{g}_{ij}$ the variation in $\mathbf{g}_{ij}$ accompanying a variation in temperature or electric field at constant strain. It is possible to select a **g** set such that $\Delta\mathbf{g}_{ij}$ is zero over all *i* and *j*, or more generally, is independent of *i* and *j*; this **g** set is provisionally referred to as "stationary." A r.s. which can be represented by a stationary **g** set is referred to as stationary. For instance, R.S. I and R.S. II in Sec. 2.5 are stationary, while R.S. III is not. A orderly and stationary **s-g** set is possible. A r.s. which can be represented by an orderly and stationary **s-g** set is orderly and stationary.

3.2. Polarization Difference due to Temperature Difference

We first consider polarization difference due to temperature difference at constant strain. An orderly and stationary **s-g** set is selected. Ranging the bk.p.v., the bd.p., and the polarization of the crystal plate, we have

$$\left.\begin{aligned} \mathbf{P}_v &= \frac{1}{v}\left\{\sum_{i,j} f_{ij}q_{ij}(\mathbf{s}_{ij}-\mathbf{g}_i) + \sum_{i,j} f_{ij}\mathbf{p}_{ij}\right\}, \\ P_f &\approx \frac{1}{v}\left\{\sum_i q_i\left(\frac{k_i+k_i'}{2}\right)d \right. \\ &\qquad \left. + \sum_i q_i(\mathbf{n}\cdot\mathbf{g}_i) + \sum_i \Theta_i q_i d\right\}, \\ P &= \mathbf{n}\cdot\mathbf{P}_v + P_f\,. \end{aligned}\right\} \tag{3.1}$$

When temperature varies from T to T^*, the symbols of the configuration parameters vary from asteriskless to asterisked ones, at constant strain and null field. It is assumed that the crystal structure does not change abruptly. It may be obvious that

$$v^* = v,\quad d^* = d,\quad k_{ij}^* = k_i,\quad k_{ij}'^* = k_i'\,. \tag{3.2}$$

(The expression $k_{ij}^* = k_i$, $k_{ij}'^* = k_i'$ can be replaced by the expression $k_{ij}^* - k_i$ and $k_{ij}'^* - k_i'$: independent of *i* and *j*. The latter is more general.) If

$$q_i^* \approx q_i \tag{3.3}$$

and

$$\textstyle\sum_k \theta_{ijk}^* \approx \Theta_i \tag{3.4}$$

for an *arbitrary* sample of a crystal plate (species), with *arbitrary* indices, of the crystal (species), then

$$\left.\begin{aligned} &\mathbf{P}_v^* = (1/v)\{\textstyle\sum_{i,j} f_{ij}^*q_{ij}^*(\mathbf{s}_{ij}^*-\mathbf{g}_i) + \textstyle\sum_{i,j} f_{ij}^*\mathbf{p}_{ij}^*\}\,, \\ &P_f^* \approx P_f,\quad P^* = \mathbf{n}\cdot\overset{*}{\mathbf{P}_v} + P_f^*\,\cdot \end{aligned}\right\} \tag{3.5}$$

It is thought that if the set of $\mathbf{s}_{ij}$ is orderly, the set of $\mathbf{s}_{ij}^*$ is also orderly. From (3.1) and (3.5), it follows that

$$P^* - P \approx \mathbf{n}\cdot(\mathbf{P}_v^* - \mathbf{P}_v)\,. \tag{3.6}$$

The left-hand side is, in itself, unconcerned with r.s., while the right-hand side is, in itself, independent of crystal-plate boundaries. The polarization difference $P^* - P$ is therefore independent of boundaries as well as r.s.

We now scrutinize this consequence. If an arbitrary r.s. is selected, not (3.6) but the general equation

$$P^* - P = \mathbf{n}\cdot(\mathbf{P}_v^* - \mathbf{P}_v) + (P_f^* - P_f)$$

is valid. The left-hand side is independent of the particular **s-g** sets selected, but it might depend on the boundaries. Supposing the **s-g** set selected is changed, then the left-hand side remains unaltered, while each term on the right-hand side may be altered. According to the previous consideration, the second term should vanish when an orderly and stationary **s-g** set is selected. We know that the second term has no direct connection with the particular representations of the r.s. The second term should, therefore, vanish when an orderly and stationary r.s. is selected (at the temperature T). The first term remaining is, in itself, independent of the boundaries; hence it is evident that the polarization difference $P^* - P$ is, originally, independent of the boundaries.

Equation (3.6) suggests that there exists a vector $\mathbf{\Pi}$ satisfying

$$P^* - P \approx \mathbf{n}\cdot\mathbf{\Pi}\ ; \tag{3.7}$$

$\mathbf{\Pi}$ is independent of r.s., crystal-plate orientation, and crystal-plate boundaries. The equation $\mathbf{P}_v^* - \mathbf{P}_v = \mathbf{\Pi}$ is valid if an orderly and stationary r.s. is selected, but if not so, it may not hold; in a nondisordered crystal, the equation is valid if a stationary r.s. is selected. (All the orderly and stationary r.s.'s give the same $\mathbf{P}_v^* - \mathbf{P}_v$. This, however, does not mean that all give the same $\mathbf{P}_v^*$ and the same $\mathbf{P}_v$.) The quantity $\mathbf{\Pi}$ is provisionally referred to as the polarization difference vector between T and T^*.

Equation (3.3) is thought to be valid for the crystal of ionic character. The validity of Eq. (3.4) might be correlated with time effect, but within an ordinary time interval, the equation may hold. If there were a crystal not satisfying (3.4), it should rather be considered a special kind of crystal that has singular surfaces and exhibits anomalies about pyroelectric coefficient, susceptibility, and so forth.

3.3. Polarization Difference due to Phase Transition

If the crystal transforms its phase at a certain temperature (under constant strain and null field), then its structure might abruptly change at the temperature. This case is considered here. That the "crystal" transforms its phase at a certain temperature should mean that the transition temperature is practically independent of crystal-plate orientation. The argument here is found analogous to that in Sec. 3.2, and so it will be briefly done. The parameter symbols are asteriskless before the change and asterisked after the change. An orderly and stationary **s-g** set is selected. The equations in (3.2) are valid. Equations (3.3) and (3.4) are thought to be valid. The argument hitherto is analogous to that in Sec. 3.2, and so the conclusion should be analogous. The equation $P_f^* \approx P_f$ holds. The polarization difference $P^* - P$ is independent of boundaries as well as r.s. There exists a vector $\mathbf{\Pi}$ satisfying (3.7); $\mathbf{\Pi}$ is independent of r.s., crystal-plate orientation, and crystal-plate boundaries. All the orderly and stationary r.s.'s give the same $\mathbf{P}_v^* - \mathbf{P}_v$, which is equal to $\mathbf{\Pi}$. Both the phases need not be disordered to the same degree. It may well happen that one phase is disordered and the other is not.

3.4. Pyroelectric Coefficient at Constant Strain

When temperature difference $T^* - T$ is reduced to an infinitesimal, the problem of a polarization difference becomes that of a pyroelectric coefficient, which is treated here. The present argument is found analogous to that in Sec. 3.2, and so it is briefly treated. An orderly and stationary **s-g** set is selected. At constant strain and null field, the equations

$$\partial q_i/\partial T \approx 0, \quad (\partial/\partial T) \textstyle\sum_k \theta_{ijk} \approx 0 \tag{3.8}$$

may be valid for an arbitrary sample of a crystal plate, with arbitrary indices, of the crystal. Therefore,

$$\frac{\partial \mathbf{P}_v}{\partial T} = \frac{1}{v}\left\{\sum_{i,j} f_{ij}q_{ij}\frac{\partial(\mathbf{s}_{ij} - \mathbf{g}_i)}{\partial T} + \sum_{i,j} f_{ij}\frac{\partial \mathbf{p}_{ij}}{\partial T} + \sum_{i,j}\frac{\partial(f_{ij}q_{ij})}{\partial T}(\mathbf{s}_{ij} - \mathbf{g}_i) + \sum_{i,j}\frac{\partial f_{ij}}{\partial T}\mathbf{p}_{ij}\right\}, \tag{3.9}$$

$$\partial P_f/\partial T \approx 0\,, \tag{3.10}$$

$$\partial P/\partial T \approx \mathbf{n}\cdot\partial\mathbf{P}_v/\partial T\,. \tag{3.11}$$

It is evident that the pyroelectric coefficient $\partial P/\partial T$ at constant strain is independent of boundaries as well as r.s., or in other words, that it is definite for the crystal plate (species). Equation (3.11) suggests that there exists a vector $\boldsymbol{\pi}$ satisfying

$$\partial P/\partial T \approx \mathbf{n}\cdot\boldsymbol{\pi}\ ; \tag{3.12}$$

$\boldsymbol{\pi}$ is definite for the crystal (species), that is, independent of r.s., crystal-plate orientation, and crystal-plate boundaries; it is provisionally referred to as the "pyroelectric vector." If a nonorderly or nonstationary r.s. is selected, the general equation

$$\partial P/\partial T = \mathbf{n}\cdot(\partial\mathbf{P}_v/\partial T) + \partial P_f/\partial T$$

should be employed instead of (3.11). If an orderly and stationary r.s. is selected, then

$$\partial\mathbf{P}_v/\partial T = \boldsymbol{\pi}\,. \tag{3.13}$$

Considering the meanings of the respective terms on the right-hand side of (3.9), the first and second terms may correspond to the effects of ionic and electronic displacement, respectively, and the last two terms, to the effect of variation in disorder.

3.5. Illustration of Orderly and Nonorderly Reference Structures

The model crystal shown in Fig. 4 serves to illustrate orderly and nonorderly r.s.'s. It consists of two kinds of ions and has disorder. The first and the second ion possess a negative charge $-q$ and a positive charge q, respectively, and have no dipoles. The fundamental translation vector **a** is normal to the paper face, **c** is parallel to that and orients from left to right horizontally, and **b** is normal to the former two. Open circles and full ones are projections of first- and second-ion positions, respectively. There are two kinds of second-ion positions. The charge of the second ion is independent of the particular kinds of positions. The first-ion positions are unique. Points A,B,C, and D are first-ion positions in a plane parallel to the paper face. At a distance **a** from them, there are points A′,B′,C′, and D′, respectively. Point E is the body center of the hexahedron ABCDA′-B′C′D′. Points F and G are the face centers of the rectangles ADA′D′ and BCB′C′, respectively. Points H and L are a (2,1) and a (2,2) position, respectively, and are situated on the line FG. Point K is distant by **c** from H. The normal vector **n** of the crystal plate is parallel to **c**. The surface parts include no vacancies and have the parameters of the same values as the central part has. We put

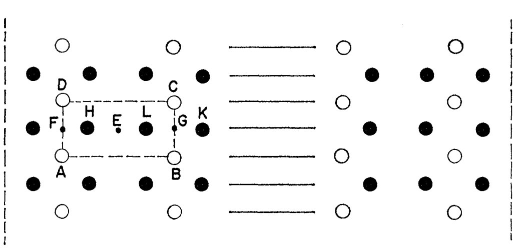

FIG. 4. Model crystal plate having disorder. The vector **a** is normal to the paper face, **c** is parallel to that and horizontal, and **b** is normal to the former two. Open circles and full ones are projections of positions of negative first ions and positive second ions, respectively. There are two kinds of second-ion positions. The surface parts include no vacancies and have the parameters of the same values as has the central part.

$$\overline{\mathrm{EH}} = u_1, \quad \overline{\mathrm{EL}} = u_2, \quad \overline{\mathrm{FH}} = w_1, \quad \overline{\mathrm{GL}} = w_2,$$

and

$$f_{21} = f, \quad f_{22} = 1 - f.$$

We set

$$\mathbf{s}_1 = 0, \quad \mathbf{g}_1 = 0.$$

Equations (2.6) and (2.7) become

$$P_v = \mathbf{n}\cdot\mathbf{P}_v = (q/v)\{f\mathbf{n}\cdot(\mathbf{s}_{21} - \mathbf{g}_{21}) + (1-f)\mathbf{n}\cdot(\mathbf{s}_{22} - \mathbf{g}_{22})\}\,,$$

$$P_f = \frac{q}{v}\left\{\left(-\frac{k_1 + k_1'}{2} + f\frac{k_{21} + k_{21}'}{2} + (1-f)\frac{k_{22} + k_{22}'}{2}\right)c + f\mathbf{n}\cdot\mathbf{g}_{21} + (1-f)\mathbf{n}\cdot\mathbf{g}_{22}\right\}.$$

R.S. α. We select

$$\mathbf{s}_{21} = \overrightarrow{\mathrm{AH}}, \quad \mathbf{s}_{22} = \overrightarrow{\mathrm{AL}}, \quad \mathbf{g}_{21} = \mathbf{g}_{22} = \overrightarrow{\mathrm{AE}}.$$

Then

$$\mathbf{s}_{21} - \mathbf{g}_{21} = \overrightarrow{\mathrm{EH}}, \quad \mathbf{s}_{22} - \mathbf{g}_{22} = \overrightarrow{\mathrm{EL}},$$

$$k_{21} = k_1, \quad k_{22} = k_1 - 1, \quad k_{21}' = k_1', \quad k_{22}' = k_1' - 1,$$

$$P_v = (q/v)\{-fu_1 + (1-f)u_2\}\,,$$

$$P_f = (q/v)(f - \tfrac{1}{2})c\,.$$

Therefore, at constant strain,

$$\frac{\partial P_v}{\partial T} = \frac{q}{v}\left\{-f\frac{\partial u_1}{\partial T} + (1-f)\frac{\partial u_2}{\partial T} - \frac{\partial f}{\partial T}(u_1 + u_2)\right\},$$

$$\partial P_f/\partial T = (q/v)\,(\partial f/\partial T)\,c\,,$$

$$\frac{\partial P}{\partial T} = \frac{q}{v}\left\{-f\frac{\partial u_1}{\partial T} + (1-f)\frac{\partial u_2}{\partial T} + \frac{\partial f}{\partial T}(c - u_1 - u_2)\right\}.$$

It is evident that

$$\partial P/\partial T \neq \partial P_v/\partial T\,.$$

This **s** set is not orderly; this r.s. is not orderly (though stationary).

R.S. β. We select

$$\mathbf{s}_{21} = \overrightarrow{\mathrm{AH}}, \quad \mathbf{s}_{22} = \overrightarrow{\mathrm{AL}}, \quad \mathbf{g}_{21} = \overrightarrow{\mathrm{AF}}, \quad \mathbf{g}_{22} = \overrightarrow{\mathrm{AG}}.$$

Then,

$$\mathbf{s}_{21} - \mathbf{g}_{21} = \overrightarrow{\mathrm{FH}}, \quad \mathbf{s}_{22} - \mathbf{g}_{22} = \overrightarrow{\mathrm{GL}},$$

$$k_{21} = k_1, \quad k_{22} = k_1 - 1, \quad k_{21}' = k_1', \quad k_{22}' = k_1' - 1,$$

$$P_v = (q/v)\{fw_1 - (1-f)w_2\}, \quad P_f = 0, \quad P = P_v.$$

Therefore,

$$\frac{\partial P}{\partial T} = \frac{\partial P_v}{\partial T} = \frac{q}{v}\left\{f\frac{\partial w_1}{\partial T} - (1-f)\frac{\partial w_2}{\partial T} + (\partial f/\partial T)(w_1 + w_2)\right\}.$$

Although this **s** set is not orderly, the equation

$$\partial P/\partial T = \partial P_v/\partial T$$

holds. The fact is that this model crystal has been so made that this r.s. is orderly. Orderly representations of this r.s. are obtained as follows. If we select

$$\mathbf{s}_{21} = \overrightarrow{\mathrm{BK}}, \quad \mathbf{s}_{22} = \overrightarrow{\mathrm{BL}}, \quad \mathbf{g}_{21} = \mathbf{g}_{22} = \overrightarrow{\mathrm{BG}},$$

then

$$\mathbf{s}_{21} - \mathbf{g}_{21} = \overrightarrow{\mathrm{GK}} = \overrightarrow{\mathrm{FH}}, \quad \mathbf{s}_{22} - \mathbf{g}_{22} = \overrightarrow{\mathrm{GL}},$$
$$k_{21} = k_{22} = k_1, \quad k'_{21} = k'_{22} = k'_1 \ ;$$

hence, this **s-g** set represents R.S. β and is orderly (at least for this orientation). If we select

$$\mathbf{s}_{21} = \overrightarrow{\mathrm{AK}}, \quad \mathbf{s}_{22} = \overrightarrow{\mathrm{AL}}, \quad \mathbf{g}_{21} = \mathbf{g}_{22} = \overrightarrow{\mathrm{AG}},$$

then

$$\mathbf{s}_{21} - \mathbf{g}_{21} = \overrightarrow{\mathrm{GK}} = \overrightarrow{\mathrm{FH}}, \quad \mathbf{s}_{22} - \mathbf{g}_{22} = \overrightarrow{\mathrm{GL}},$$
$$k_{21} = k_{22} = k_1 - 1, \quad k'_{21} = k'_{22} = k'_1 - 1 \ ;$$

hence, this **s-g** set also represents R.S. β and is orderly. (Incidentally, R.S. β is stationary.)

3.6. Susceptibility at Constant Strain

An orderly and stationary **s-g** set is selected. When an infinitesimal electric field (normal to the crystal plate) is applied at constant temperature and constant strain, it may be obvious that

$$\partial v/\partial E = \partial d/\partial E = \partial k_{ij}/\partial E = \partial k'_{ij}/\partial E = 0 \ . \tag{3.14}$$

where E is electric field. The equations

$$\partial q_i/\partial E \approx 0, \quad (\partial/\partial E) \textstyle\sum_k \theta_{ijk} \approx 0 \tag{3.15}$$

are thought to be *always* valid. Therefore, it is evident that

$$\partial P_f/\partial E \approx 0, \quad \partial P/\partial E \approx \mathbf{n}\cdot\partial\mathbf{P}_v/\partial E \ . \tag{3.16}$$

If the tensor

$$\frac{\partial\mathbf{P}_v}{\partial\mathbf{E}} \equiv \begin{pmatrix} \partial P_{vx}/\partial E_x & \partial P_{vx}/\partial E_y & \partial P_{vx}/\partial E_z \\ \partial P_{vy}/\partial E_x & \partial P_{vy}/\partial E_y & \partial P_{vy}/\partial E_z \\ \partial P_{vz}/\partial E_x & \partial P_{vz}/\partial E_y & \partial P_{vz}/\partial E_z \end{pmatrix} \tag{3.17}$$

is employed (x,y,z refer to the axes of an arbitrary Cartesian coordinate system, and P_{vx} is the component of $\mathbf{P}_v$ in the x direction), then

$$\partial\mathbf{P}_v/\partial E = (\partial\mathbf{P}_v/\partial\mathbf{E})\mathbf{n} \tag{3.18}$$

(the total differentiability has been assumed); hence, (3.16) becomes

$$\partial P/\partial E \approx \mathbf{n}(\partial\mathbf{P}_v/\partial\mathbf{E})\mathbf{n} \ . \tag{3.19}$$

The left- and the right-hand sides are independent of r.s. and boundaries, respectively; hence, the susceptibility $\partial P/\partial E$ should be independent of boundaries as well as r.s., or in other words, be definite for the crystal plate (species). Equation (3.19) suggests that there exists a symmetrical tensor $\tilde{\chi}$ satisfying

$$\partial P/\partial E \approx \mathbf{n}\tilde{\chi}\mathbf{n} \ ; \tag{3.20}$$

$\tilde{\chi}$ is unique and independent of r.s., crystal-plate orientation, and crystal-plate boundaries; or it is definite for the crystal (species). If an orderly and stationary r.s. is selected, then

$$[\tilde{\chi}]_{ij} = \tfrac{1}{2}\,(\partial P_{vi}/\partial E_j + \partial P_{vj}/\partial E_i)\,(i,j = x,y,z) \ . \tag{3.21}$$

The crystal constant $\tilde{\chi}$ is known as susceptibility tensor at constant strain.

Selecting an orderly and stationary **s-g** set, and writing

$$\mathbf{n}\cdot\mathbf{P}_v = P_v, \ \mathbf{n}\cdot\mathbf{s}_{ij} = s_{ij}, \ \mathbf{n}\cdot\mathbf{g}_i = g_i, \ \mathbf{n}\cdot\mathbf{p}_{ij} = p_{ij} \ , \tag{3.22}$$

then we have

$$\frac{\partial P}{\partial E} \approx \frac{\partial P_v}{\partial E} = \frac{1}{v}\left\{\sum_{i,j} f_{ij}q_{ij}\,\frac{\partial(s_{ij} - g_i)}{\partial E} + \sum_{i,j} f_{ij}\frac{\partial p_{ij}}{\partial E} + \sum_{i,j}\frac{\partial(f_{ij}q_{ij})}{\partial E}(s_{ij} - g_i) + \sum_{i,j}\frac{\partial f_{ij}}{\partial E}p_{ij}\right\} . \tag{3.23}$$

The first and second terms on the right-hand side correspond to the effects of ionic and electronic displacement, respectively, and the last two terms, to the effect of change in disorder. If a nonorderly or nonstationary r.s. is selected, the general equation

$$\partial P/\partial E = \partial P_v/\partial E + \partial P_f/\partial E$$

should be employed.

4. PYROELECTRIC COEFFICIENT AND SUSCEPTIBILITY AT NULL STRESS

4.1. Pyroelectric Vector and Susceptibility Tensor at Null Stress

At null stress, the space lattice of the crystal may be deformed when the temperature or the electric field varies; on this account the arguments at "null stress" become different from those at "constant strain." In some cases the deformation is very little; for instance, the space lattice of the non-piezoelectric crystals is deformed very little by the electric field, and there are some crystals in which the space lattice is deformed very little when temperature varies within some limits. In these cases the arguments, even though at null stress, can be done analogously to those in Sec. 3, and so need not be repeated. Much deformation of the space lattice is allowed for in this chapter.

We saw in Sec. 3 that, at constant strain, the pyroelectric coefficient π or the susceptibility χ of a crystal plate, with arbitrary indices, of a crystal is equal to the component of the pyroelectric vector $\boldsymbol{\pi}$ or the susceptibility tensor $\tilde{\chi}$ of the crystal in the normal ($\mathbf{n}$) direction of the crystal plate, that is,

$$\pi = \mathbf{n}\cdot\boldsymbol{\pi}, \quad \chi = \mathbf{n}\tilde{\chi}\mathbf{n}\,. \tag{4.1}$$

These relations are essential to $\boldsymbol{\pi}$ and $\tilde{\chi}$. At null stress, π and χ can again be defined, as will shortly be seen, but $\boldsymbol{\pi}$ and $\tilde{\chi}$ such as satisfy (4.1) over all possible $\mathbf{n}$ are not generally present.

For the illustration we consider the pyroelectric coefficient of a model crystal belonging to the point group *m*. It consists of two kinds of dipoleless ions. Distant by $\mathbf{s}$ from a negative ion, there is a positive ion. The direction of $\mathbf{s}$ is parallel to the [101] axis at any temperature. The magnitude s of $\mathbf{s}$ and the angle β between the [100] and [001] axes vary with temperature. Supposing $\boldsymbol{\pi}$ exists, the crystal symmetry requires parallelism of $\boldsymbol{\pi}$ to the (010) plane. The pyroelectric coefficient of the $(10\bar{1})$ crystal plate is to be observed as zero (see Sec. 4.3), so that $\boldsymbol{\pi}$ must be parallel to the [101] axis, from (4.1). The pyroelectric coefficient of the (001) crystal plate might be observed as nearly zero or as far from zero. We suppose that it is accidentally zero. (This is possible if there is a certain relation between $\partial s/\partial T$ and $\partial\beta/\partial T$.) Then $\boldsymbol{\pi}$ must be parallel to the [100] axis, from (4.1). Thus, eventually $\boldsymbol{\pi}$ must be zero. But on the other hand, the pyroelectric coefficient of the (101) crystal plate may in general be observed as nonzero. Thus, here is a contradiction.

Such a contradiction is general and not peculiar to the above model crystal. From (4.1), $\boldsymbol{\pi}$ can be determined by observing the pyroelectric coefficients in three linearly-independent directions $\mathbf{n}_1$,$\mathbf{n}_2$, and $\mathbf{n}_3$ (fewer directions are often sufficient if crystal symmetry is taken into account); this $\boldsymbol{\pi}$ might not satisfy (4.1) with respect to a fourth direction $\mathbf{n}_4$. It is noted that, at null stress, the relation (4.1) is more or less approximate depending on the degree of lattice deformation. At constant strain we treated "crystals"; but at null stress, for the above reason, we shall treat only "crystal plates," or not connect each crystal plate with its infinite crystal.

4.2. Polarization Difference at Null Stress

If we write

$$\mathbf{n}\cdot\mathbf{P}_v = P_v, \;\; \mathbf{n}\cdot\mathbf{s}_{ij} = s_{ij}, \;\; \mathbf{n}\cdot\mathbf{g}_{ij} = g_{ij}, \;\; \mathbf{n}\cdot\mathbf{p}_{ij} = p_{ij}, \tag{4.2}$$

then (2.6), (2.10), and (2.8) become, respectively,

$$P_v = \frac{1}{v}\left\{\sum_{i,j} f_{ij}q_{ij}(s_{ij} - g_{ij}) + \sum_{i,j} f_{ij}p_{ij}\right\}, \tag{4.3}$$

$$P_f = \frac{1}{v}\left\{\sum_{i,j} f_{ij}q_{ij}\left(\frac{k_{ij} + k'_{ij}}{2}\right)d + \sum_{i,j} f_{ij}q_{ij}g_{ij} + \sum_{i,j,k} \theta_{ijk}f_{ij}q_{ij}d\right\}, \tag{4.4}$$

$$P = P_v + P_f\,. \tag{4.5}$$

These new forms do not contain any vectors. Now, the new scalar parameters s_{ij}, p_{ij}, etc., should be conceived as the components of $\mathbf{s}_{ij}$, $\mathbf{p}_{ij}$, etc., in the direction "normal to the crystal plate" rather than "of $\mathbf{n}$." (There is a *nuance* between both. The latter is connected with the infinite crystal, while the former is not.)

In the present case also, it is convenient to employ "reference structure," "orderly" r.s., and "stationary" r.s. If the set of s_{ij} and g_{ij} and the set of s^*_{ij} and g^*_{ij} are representative of the same r.s., then it is conceived that $s^*_{ij} - g^*_{ij} = s_{ij} - g_{ij} + A$ for all i and j, where A is a constant. An s set is referred to as orderly, when it makes

k_{ij},k^*_{ij}, *and* $\sum_k\theta_{ijk}$ *quite, or almost, independent of j,*

or

$$k_{ij} = k_i, \quad k'_{ij} = k'_i, \quad \sum_k \theta_{ijk} \approx \Theta_i\,, \tag{4.6}$$

for an *arbitrary* sample of the crystal plate (species), at a given temperature and null field. When, in addition, g_{ij} are selected so that they are independent of j or $g_{ij} = g_i$, the set of s_{ij} and g_{ij} is referred to as orderly. A r.s. is referred to as orderly, when it can be represented by an orderly *s-g* set. In a crystal plate without disorder, any *s-g* set or any r.s. is orderly. If an orderly *s-g* set is selected, Eq. (4.4) is reduced to

$$P_f \approx \frac{d}{v}\left\{\sum_i q_i\left(\frac{k_i + k'_i}{2}\right) + \sum_i q_i\left(\frac{g_i}{d}\right) + \sum_i \Theta_i q_i\right\}, \tag{4.7}$$

where q_i is defined by (2.13). We denote by $\Delta(g_{ij}/d)$ the variation in g_{ij}/d accompanying a variation in temperature or electric field at null stress. It is possible to select a g set such that $\Delta(g_{ij}/d)$ is zero for all i and j, or more generally, is independent of i and j; this g set is referred to as stationary. A r.s. which can be represented by a stationary g set is referred to as stationary.

We consider polarization difference due to temperature difference or field difference. When temperature or field varies from X (= 0 in case of field) to X^*, the symbols of the configuration parameters of the crystal plate vary from asteriskless to asterisked ones. An orderly and stationary *s-g* set is selected. It may be obvious that

$$k^*_{ij} = k_i, \quad k'^*_{ij} = k'_i \,. \tag{4.8}$$

For an arbitrary sample, the equations

$$q^*_i \approx q_i \tag{4.9}$$

and

$$\textstyle\sum_k \theta^*_{ijk} \approx \Theta_i \tag{4.10}$$

may hold. (If the set of s_{ij} is orderly, the set of s_{ij} may be so.) From the above, it follows that

$$(v^*/d^*)P^*_f \approx (v/d)P_f \,, \tag{4.11}$$

$$P^* - P \approx (P^*_v - P_v) + (d^*/v^* \cdot v/d - 1)P_f \,. \tag{4.12}$$

If γ denotes the average rate of square expansion of the main face of the crystal plate between X and X^*, Eq. (4.12) is rewritten to

$$P^* - P \approx (P^*_v - P_v) - (X^* - X)\gamma P_f \,. \tag{4.13}$$

We now turn from the problem of polarization difference to the problems of pyroelectric coefficient and susceptibility.

4.3. Pyroelectric Coefficient and Susceptibility at Null Stress

When $T^* - T$ or E^* is reduced to an infinitesimal, the argument of polarization difference becomes that of pyroelectric coefficient or susceptibility, the infinitesimal differences being replaced by the differential coefficients. We denote the differential of temperature or field by dX. Selecting an orderly and stationary r.s., we have from (4.13)

$$\partial P/\partial X \approx \partial P_v/\partial X - \gamma P_f \,, \tag{4.14}$$

where

$$\gamma = (\partial/\partial X) \log (v/d) \,,$$

that is, γ is the rate of thermal or piezoelectric square expansion of the main face of the crystal plate at the temperature T and null field.

In case γ is not zero, $\partial P/\partial X$ might depend on boundaries, or in other words, its observed values might vary according to samples of the crystal plate. The extent, however, of this variation is material. It might, or might not, be so small that $\partial P/\partial X$ is practically thought a crystal-plate constant. We denote the extent of variation in $\partial P/\partial X$ by $\Delta(\partial P/\partial X)$. The bk.p. is independent of boundaries, so that

$$\Delta(\partial P/\partial X) = \gamma \Delta P_f = \gamma \Delta P \,, \tag{4.15}$$

where ΔP is the extent of variation in P at null field. From (4.15) it follows that if γ or ΔP is small, $\Delta(\partial P/\partial X)$ is so. We are first concerned with susceptibility. In the nonpiezoelectric crystal, γ is nearly zero, and so it is evident that $\Delta(\partial P/\partial E) \approx 0$. In a piezoelectric crystal, γ might not be near to zero, and so ΔP should be examined.

We are next concerned with pyroelectric coefficient. Since γ is generally nonzero, ΔP must be examined. Among crystal plates, there are those which can exhibit large polarizations at null field, while there are those which exhibit only nearly-zero polarizations. In the latter crystal plates, ΔP is nearly zero, and so it is evident that $\Delta(\partial P/\partial T) \approx 0$. In the former crystal plates, the observed values of P may range from 0 to $P_{\max}$ in accordance with samples, and so $\Delta P \approx P_{\max}$. The expansion rate γ is, ordinarily, of the order of 10^{-5} deg^{-1}. Hence, $\Delta(\partial P/\partial T) \approx 10^{-5}$ deg^{-1} $\times P_{\max}$. In order to see the order of $\Delta(\partial P/\partial T)$, we refer to two examples. They are the crystal plates, normal to the polar axis, of barium titanate and GASH. (GASH is the abbreviation of guanidinium aluminum sulfate hexahydrate.) Their ferroelectric spontaneous polarization (see Sec. 6.3) is denoted by P_s. Then, it may be reasonable to put $P_{\max} \approx 2P_s$. At room temperature, thus, for barium titanate $\Delta(\partial P/\partial T) \approx 5 \times 10^{-4}$ μC cm^{-2} deg^{-1} ($P_s = 26$ μC cm^{-2}), and for GASH $\Delta(\partial P/\partial T) \approx 7 \times 10^{-6}$ μC cm^{-2} deg^{-1} ($P_s = 0.35$ μC cm^{-2}). It is seen that values of $\Delta(\partial P/\partial T)$ fairly differ according to crystal plates (species). In practice the ratio of $\Delta(\partial P/\partial T)$ to $-\partial P/\partial T$ is more important. For barium titanate, $-\partial P/\partial T \approx 3 \times 10^{-2}$ μC cm^{-2} deg^{-1}, and for GASH, $-\partial P/\partial T \approx 1.5 \times 10^{-3}$ μC cm^{-2} deg^{-1}; hence it is evident that $\Delta(\partial P/\partial T)$ is fairly small compared with $-\partial P/\partial T$. These pyroelectric coefficients at null stress are, therefore, practically thought to be crystal-plate constants.

From the above considerations, it may be concluded that the pyroelectric coefficient at null stress is, ordinarily, a crystal-plate constant. As to susceptibility and polarization difference, similar conclusions will hold.

4.4. Ordinary Boundaries

A crystal plate (species) possessing "ordinary" boundaries (in a pair) has such an orderly and stationary r.s. as gives *ordinarily* $P_f \approx 0$ (see Sec. 2.6). Selecting such a r.s., the equations

$$P \approx P_v, \quad P^* \approx P^*_v \tag{4.16}$$

ordinarily hold since the bd.p. P^*_f at the temperature T^* is also ordinarily zero, from (4.11).

We consider what is meant by an "ordinary" sample. What sort of sample is ordinary is not so clear. Different processes of making samples might yield different characters of samples; for instance, whether the field inside the growing crystal was zero, steadily strong, or variable; whether we prepared the crystal plate in the nonpolar phase at a high temperature and then cooled it down to the polar phase at room temperature, or we prepared the crystal plate in the polar phase at a temperature and then brought it to room temperature, or we made the crystal plate at room temperature originally. Some crystal plate might not be sensitive to a difference in making-processes, and on this account, all its available samples might have a like boundary-pair. In some other crystal plate, all its available samples might be made through one dominant process exclusively, and on this account might have a like boundary-pair. In such a crystal plate, however, if another more advantageous process of making becomes discovered and expels the previous one, and if the crystal plate is sensitive to a difference in making-processes, then its "ordinary" boundaries will become otherwise.

As an example, we consider the (001) crystal plate of barium titanate at room temperature. Its samples are, currently, manufactured through the following process. First, a plate is prepared in the cubic phase at a higher temperature than 120°C under null field, and then it is cooled down to the polar phase at room temperature. In the cubic phase, since opposite senses of the normal are equivalent (in symmetry), both its boundaries may be identical, and therefore the polarization may be zero at null field. If we select such a r.s. as gives zero bk.p. in the cubic phase, P_f may be zero in both the phases.

The crystal plates which can exhibit a large polarization at null field are thought sensitive to a difference in making-processes. Their samples which exhibit a large polarization at a temperature cannot be manufactured *in a state of nature* at that temperature originally (owing to a large depolarization field).

5. PYROELECTRICITY AND SPONTANEOUS POLARIZATION

5.1. Spontaneous Polarization Vector

When a crystal plate, with certain indices, of a crystal has a nonzero pyroelectric coefficient at null field under constant strain or null stress, the crystal plate or the crystal is said to be "pyroelectric" or to exhibit "pyroelectricity." As is well known, all crystals are classified, according to their symmetries, into 32 point groups, of which 21 are noncentrosymmetrical groups, of these 21, ten are polar groups. (A crystal belonging to a polar group is also termed a polar crystal.)

In association with "pyroelectricity," the following conception might be held (in fact, it has often been held). Just as the ferromagnetic crystal possesses a "spontaneous magnetization vector," the pyroelectric crystal should possess a ⟨spontaneous polarization vector⟩ (briefly, ⟨s.p.v.⟩) as a characteristic quantity. The cause of pyroelectricity of the crystal should be the variation of this ⟨s.p.v.⟩ with temperature. The pyroelectric crystal should be polar (because a crystal having a nonzero ⟨s.p.v.⟩, if any, must be polar, from symmetry).

Or rather, another more general conception might be held. Any polar crystal should possess a ⟨s.p.v.⟩. This would more or less vary with temperature. Therefore, any polar crystal should more or less exhibit pyroelectricity. Thus it follows that the "pyroelectric crystals" and the "polar crystals" should be synonymous.

It is noticed that the above conceptions are not to be immediately connected with the original definition of the "pyroelectric crystal." We examine the concept of ⟨s.p.v.⟩. The ⟨s.p.v.⟩, as is conceived, of a crystal in a certain state is one of the bk.p.v.'s (termed so in this paper) and is uniquely determined solely by the charge configuration inside the crystal in that state. How true is this conception? Seeing (2.6), the second term is independent of r.s., but the first is not. In the magnetic crystal that contains no separate "magnetic charges," the bk.p.v. comprises the second term alone, and so it is independent of r.s., or only one bk.p.v. is present. The molecular dielectric crystal is analogous, in this respect, to the magnetic crystal (see Sec. 2.7). In these crystals, ⟨s.p.v.⟩ (or "spontaneous magnetization vector") is, therefore, naturally definite. In the ionic dielectric crystal, however, since the bk.p.v. contains the first term and so varies with r.s., the ⟨s.p.v.⟩ is not naturally definite. Thus, the ionic dielectric crystal does not possess ⟨s.p.v.⟩ of the same nature as that which the magnetic crystal and the molecular dielectric crystal possess. But it might be conceived that, among various bk.p.v.'s of the ionic dielectric crystal, there must be some special one appropriate for the ⟨s.p.v.⟩. If one attempts to seek it out, one must first of all select the property with which to determine the speciality of the respective bk.p.v.'s It is now supposed that one property has been selected. When the speciality is judged according to that property, more than one different bk.p.v.'s might be equally special. Then, it would be necessary to invoke another property, in order to determine which one of them is more special than any other. It may be natural to select "symmetry" as the criterion property. This property has a complete effect, however, solely on the nonpolar crystals. For them, zero bk.p.v. is more special than any other, so that it may be reasonable to define their ⟨s.p.v.⟩ as zero. For the crystals belonging to the polar groups except 1 and *m*, the symmetry operation determines merely the direction of their ⟨s.p.v.⟩, and not its magnitude nor sense. For the crystals belonging to 1 and *m*, even the direction cannot be determined. In order to complete the definition of ⟨s.p.v.⟩, therefore, other properties are necessary in addition to symmetry. It might be possible to make the general rule for determining the ⟨s.p.v.'s⟩ of all crystals; such ⟨s.p.v.'s⟩ would, however, be more or less arbitrary. From the above, we see it unreasonable to postulate a definite ⟨s.p.v.⟩ for every polar crystal of ionic character.

As to some pyroelectric crystals and some ferroelectric crystals, their "observed s.p.v.'s" have been reported. This might be thought to contradict the above consideration. But it will soon become clear that pyroelectric s.p.v. and ferroelectric s.p.v. are different, in nature, from previous ⟨s.p.v.⟩, and moreover that the pyroelectric one has a different nature from that of the ferroelectric one. Various natures of s.p.v.'s might be conceived; one of them might, or might not, be equal in value to another.

5.2. Symmetry of Pyroelectric Crystals and Pyroelectric Spontaneous Polarization Vector

In this section, we are concerned with the crystal exhibiting pyroelectricity at constant strain. According to Sec. 3.4, this crystal has a nonzero pyroelectric vector, and therefore must be polar, from symmetry. Thus, it is not the ⟨s.p.v.⟩ but the "pyroelectric vector" that requires the crystal to be polar.

We attempt to define the s.p.v. of the crystal. The s.p.v. is supposed to exist, and is denoted by $\mathbf{P}_s(T,\sigma)$ since it may depend on the temperature T and the strain σ. The pyroelectric vector is denoted by $\boldsymbol{\pi}(T,\sigma)$. Then, from the meaning of the pyroelectric s.p.v., the equation

$$\partial \mathbf{P}_s(T,\sigma)/\partial T = \boldsymbol{\pi}(T,\sigma) \tag{5.1}$$

should hold. Integrating both sides with respect to temperature, we obtain

$$\mathbf{P}_s(T,\sigma) = \mathbf{P}_s(T^*,\sigma) + \int_{T^*}^{T} \boldsymbol{\pi}(T',\sigma)\mathrm{d}T' , \tag{5.2}$$

where T^* is a certain temperature. The vector $\mathbf{P}_s(T^*,\sigma)$ should be independent of r.s., crystal-plate orientation, and crystal-plate boundaries, since $\boldsymbol{\pi}(T',\sigma)$ is so and $\mathbf{P}_s(T,\sigma)$ should be so. However, it is obvious that $\mathbf{P}_s(T^*,\sigma)$ is undefinable except in the following case.

This case is that, at the strain σ and null field, the crystal has a phase transition at a temperature $T_t(\sigma)$ and belongs to a nonpolar group in one phase n and exhibits pyroelectricity in the other phase p. The transition temperature $T_t(\sigma)$ may depend on σ. It is assumed that the parameters, $\mathbf{s}_{ij}$ etc., are continuous at $T_t(\sigma)$. If T^* is a temperature in n phase, $\mathbf{P}_s(T^*,\sigma)$ must be zero (from symmetry), so that the equation

$$\mathbf{P}_s(T,\sigma) = \int_{T^*}^{T} \boldsymbol{\pi}(T',\sigma)\mathrm{d}T' \tag{5.3}$$

must hold. (At any temperature T' between $T_t(\sigma)$ and T^*, $\boldsymbol{\pi}(T',\sigma) = 0$. The temperature T is in p phase.) In this case, thus, $\mathbf{P}_s(T,\sigma)$ is uniquely defined in terms of $\boldsymbol{\pi}(T',\sigma)$. From Sec. 3.2 and 3.4, it is obvious that

$$\boldsymbol{\Pi}(T,T^*,\sigma) = \int_{T}^{T^*} \boldsymbol{\pi}(T',\sigma)\mathrm{d}T' . \tag{5.4}$$

Hence the equation

$$\mathbf{P}_s(T,\sigma) = \boldsymbol{\Pi}(T^*,T,\sigma) \tag{5.5}$$

also holds. The s.p.v. could have also been defined in terms of the polarization difference vector. If we select such an orderly and stationary r.s. as gives zero bk.p.v. in n phase at the strain σ, then we have

$$\mathbf{P}_s(T,\sigma) = \mathbf{P}_v(T,\sigma) , \tag{5.6}$$

from (5.5) and Sec. 3.2.

As to some pyroelectric crystals having a phase transition to a nonpolar phase, their "observed s.p.v.'s" have been reported. We now notice that they are of the same nature as that of the s.p.v. defined here. This s.p.v., however, should not be conceived the same as ⟨s.p.v.⟩ (in Sec. 5.1). The former is not *a priori* postulated but defined by (5.3), (5.5), or (5.6); it is significant solely for the pyroelectric crystals having a phase transition to a nonpolar phase; it is not determined by the internal charge configuration at the temperature, alone, but by the configuration at the temperature and the configuration in the nonpolar phase and the connection between these configurations.

5.3. Crystals without any Orderly Reference Structure

In this paper, it is assumed that every crystal has orderly **s** sets (see Sec. 2.8). If a crystal did not have any orderly **s** set, our argument would not apply to it. It may be informative to present a model crystal without any orderly **s** set. This is shown in Fig. 5. It consists of two kinds of ions and has disorder and belongs to the point group $\bar{6}$ at null field. The first and the second ion possess a negative charge $-q$ and a positive charge q, respectively, and have no dipoles. The threefold axis is normal to the paper face. The fundamental translation vector **c** is parallel to the threefold axis. Open circles are projections of first-ion positions; full circles and hatched ones are projections of (2,1) and (2,2) positions, respectively. The first-ion positions are unique. Points A,B,C,D, and E are first-ion positions in a plane parallel to the paper face. Points F and K are distant by $\mathbf{c}/2$ from the centers of the regular triangles ACD and ABC, respectively. Points F $\sim$ N are in a plane parallel to the paper face; F,G, and H are (2,1) positions, and K,L,M, and N are (2,2) positions. If f is the probability that the second ion occupies the first position, then $1-f$ is the probability that the second ion occupies the second position. Especially at $f=1/2$, the threefold axis becomes the sixfold axis. It is assumed that $f \neq 1/2$. We now watch a second ion at F. This will soon move to a second position, but the new point can be K,L, or M with an equal probability. Hence, this crystal is not thought to have any orderly **s** set. We imagine the crystal plate with its main faces parallel to the plane which goes through the line AB normally to the paper face. If f varies with temperature at constant strain, this crystal plate will exhibit pyroelectricity at constant strain. But yet it is not polar. This is inconsistent with the conclusion, in Sec. 5.2, that the crystals exhibiting pyroelectricity at constant strain must belong to the polar groups. As illustrated by this model crystal, some conclusions in this paper do not apply to crystals having no orderly **s** sets.

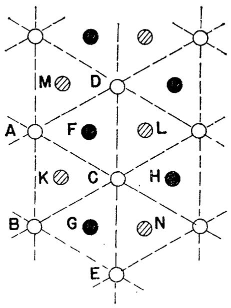

FIG. 5. Model crystal belonging to the point group $\bar{6}$ and having disorder. The threefold axis is normal to the paper face. Open circles are projections of positions of negative first ions. Full circles and hatched ones are projections of first and second positions of positive second ions, respectively.

5.4. Polarization Difference Vector and Pyroelectric Spontaneous Polarization Vector

It is supposed that at constant strain and null field a given crystal has a transition between two phases α and β, and that at the transition from α to β the parameters of the crystal vary from $\mathbf{s}_{ij}$, etc., to $\mathbf{s}^*_{ij}$, etc. At the reverse transition from β to α, the parameters might not necessarily return from $\mathbf{s}^*_{ij}$, etc., to $\mathbf{s}_{ij}$, etc. (At the transition from α to β, the parameters necessarily turn from $\mathbf{s}_{ij}$, etc., to $\mathbf{s}^*_{ji}$, etc.) The polarization difference vector $\mathbf{\Pi}$ due to the phase transition (see Sec. 3.3) is considered to be characteristic of α phase. Hence, α phase must be polar, from symmetry; if it were not so, $\mathbf{\Pi}$ should be zero. If α phase belongs to one of the polar groups except 1 and m, $\mathbf{\Pi}$ must be parallel to the polar axis. β phase may belong to a nonpolar group.

We consider, for instance, the case that α and β phases belong to point groups 2 and $2/m$, respectively. Opposite senses of the twofold axis in α are not equivalent; one of them is temporarily referred to as positive, and the other as negative, according to some property. When the crystal changes from α to β, opposite senses of the twofold axis (whose direction is invariable) become equivalent, and the distinction between the positive and negative senses vanishes. When the crystal returns from β to α, the two senses become again distinct. But the previous positive sense does not necessarily become again positive; the previous negative sense might become the new positive sense; or rather, many domains might arise.

In Sec. 5.2 we defined the s.p.v. of the pyroelectric crystal having a phase transition to a nonpolar phase; on that occasion it was assumed that the parameters $\mathbf{s}_{ij}$, etc., were continuous at the transition temperature $T_t(\sigma)$. This restriction is, now, taken off. It is thought that the pyroelectric phase and the nonpolar one correspond to above-mentioned α and β phases, respectively. Hence the pyroelectric phase at the strain σ and the temperature $T_t(\sigma)$ possesses the polarization difference vector due to the phase transition, $\mathbf{\Pi}(\sigma)$, as a characteristic quantity. It may be reasonable to define the s.p.v. of the pyroelectric phase at σ and $T_t(\sigma)$ as $-\mathbf{\Pi}(\sigma)$. Consequently, the s.p.v., $\mathbf{P}_s(T,\sigma)$, of the pyroelectric crystal at σ and T should be defined by

$$\mathbf{P}_s(T,\sigma) = -\mathbf{\Pi}(\sigma) + \int_{Tt(\sigma)}^{T} \boldsymbol{\pi}\,(T',\sigma)dT', \tag{5.7}$$

instead of (5.3). If (5.4) is used, Eq. (5.7) can be rewritten to

$$-\mathbf{P}_s(T,\sigma) = \mathbf{\Pi}(\sigma) + \mathbf{\Pi}(T,T_t(\sigma),\sigma) = \mathbf{\Pi}(T,T^*,\sigma)\ , \tag{5.8}$$

where T^* is an arbitrary temperature in the nonpolar phase. If we select such an orderly and stationary r.s. as gives zero bk.p.v. in the nonpolar phase at the strain σ, then the equation

$$\mathbf{P}_s(T,\sigma) = \mathbf{P}_v(T,\sigma) \tag{5.9}$$

is established.

5.5. Pyroelectricity and Spontaneous Polarization at Null Stress

In this section, we consider the crystal plate at null stress. A crystal plate (species) will henceforth be termed *normally nonpolar* or *polar*, according to whether opposite senses of the normal are internally equivalent or not. Since the pyroelectric coefficient $\partial P/\partial T$ at null stress is ordinarily a crystal-plate constant (see Sec. 4.3), a pyroelectric crystal plate (species) must be normally polar and hence belong to a noncentrosymmetrical group. (The crystal plates of the crystal belonging to a centrosymmetrical group are all normally nonpolar.)

We attempt to define the s.p. of that crystal plate which changes from a phase α to another phase β at a certain temperature under null stress and null field, and which is normally nonpolar in β. Considering that the polarization difference $P - P^*$ (asterisked and asteriskless symbols refer to β and α phases, respectively) is ordinarily a crystal-plate constant, it may be reasonable to define the s.p. in α as

$$P_s' = P - P^*\ . \tag{5.10}$$

In this definition, the s.p. in β has been assumed zero; it may be natural, from symmetry.

All the orderly and stationary r.s.'s giving zero bk.p. in β give the same bk.p. P_v in α (see Sec. 4.2). Hence, it may also be reasonable to define the s.p. in α as

$$P_s = P_v\ . \tag{5.11}$$

Between P_s and P_s', there is the relation

$$P_s' \approx P_s + (T^* - T)\gamma' P^*\ ,$$

from (4.13), (5.10), and (5.11); γ' is the average rate of square expansion between T and T^*. The quantity $(T^* - T)\gamma'$ may ordinarily be below 10^{-2}. Therefore, even if $P^* \approx -P_s$, the second term on the right-hand side may be fairly small compared with the first term, so that P_s and P_s' may ordinarily be almost equal. To be exact, however, P_s' depends on boundaries to some extent, while P_s does not at all. Therefore, if exactness is required, it is more desirable to define the s.p. as P_s.

Between $\partial P/\partial T$ and $\partial P_s/\partial T$, there is the relation

$$\partial P/\partial T \approx \partial P_s/\partial T - \gamma(v^*d/vd^*)P^*\ , \tag{5.12}$$

from (4.11), (4.14), and (5.11); γ is the rate of square expansion at the temperature T. Hence $\partial P/\partial T$ and $\partial P_s/\partial T$ may ordinarily be almost equal. To be exact, $\partial P/\partial T$ depends on boundaries to some extent, while $\partial P_s/\partial T$ does not at all. We have hitherto been terming $\partial P/\partial T$ the "pyroelectric coefficient." In respect to exactness, it seems more desirable to term $\partial P_s/\partial T$ as such. This way, however, presupposes the existence of P_s and so it fails in generality.

There is a quantity π' independent of r.s. as well as boundaries; it satisfies

$$\pi' = (d/v)(\partial/\partial T)[(v/d)P_v]\ , \tag{5.13}$$

if an orderly and stationary r.s. is selected. Between π' and $\partial P/\partial T$, there is the relation

$$\partial P/\partial T \approx \pi' - \gamma P\ , \tag{5.14}$$

from (4.14) and (5.13). It is also possible to define the "pyroelectric coefficient" as π'; this way is general, for, the pyroelectric crystal plate need not become normally nonpolar at a certain temperature. Ordinarily, π' and $\partial P/\partial T$ may be practically equal so that it may matter little which is designated as the pyroelectric coefficient.

The crystals, pyroelectric at constant strain, were seen to belong to the polar groups. The crystals, fairly pyroelectric at null stress, are thought to be also pyroelectric at constant strain and hence to belong to the polar groups.

6. FERROELECTRICITY

6. 1. Definition of Ferroelectricity

Ferroelectricity has often been defined as follows: A crystal is said to be ferroelectric or to exhibit ferroelectricity, when it has ⟨s.p.v.⟩ (see Sec. 5.1) and when a crystal plate, with certain indices, of it exhibits a field vs. polarization hysteresis. From this definition, it follows at once that the ferroelectric crystal should be polar. This definition, however, presupposes the existence of ⟨s.p.v.⟩. It is improper, as we saw in Sec. 5.1. Therefore, we cannot adopt this definition. Checking any crystal reported to be ferroelectric, it is found that what has been reported is not that the crystal has ⟨s.p.v.⟩, but only that a crystal plate, with certain indices, of it has two stable states of different polarizations at null field. (When a "state" of a crystal plate is spoken of, not merely the interior but also the boundaries are taken into account; two states might be identical in the interior but distinct in the boundaries. This "state" is not the same as thermodynamical "state.") To "exhibit a field vs polarization hysteresis" is, essentially, nothing but to "alternate between the two stable states by means of suitable electric field alternating." In this paper, therefore, ferroelectricity is redefined as follows. When a crystal plate, with certain indices, of a crystal has two stable states of different polarizations at null field and alternates between the states by means of suitable electric field alternating (normal to the main faces), then the crystal plate or the crystal is said to be ferroelectric or to exhibit ferroelectricity; the crystal plate must have the same crystal structure and the same thickness in the two stable states. Should the two states have an equal polarization, the field would not do any work at the state transition, or the state alternation by means of the field would not be possible. Hence, the phrase "of different polarizations" within the definition is omissible. "Two stable states" are, usually, those at null stress.

6.2. Symmetry of Ferroelectric Crystals

The two stable states of the ferroelectric crystal plate are symbolized by S_0 and S_1 for the present; the crystal plate changes from S_0 to S_1 by means of a positive field and from S_1 to S_0 by means of a negative field. When a negative or weak positive field is applied to the crystal plate in S_0, its charge configuration is uniformly modified, and when the field is taken off, the charge configuration becomes as it was originally; such modified states are also referred to as S_0. (The state S_1 is considered similar.) Once the crystal plate has changed from S_0 to S_1 by means of a positive field, it does not return to S_0 when the field is taken off.

We investigate the relationship between ferroelectricity and crystal symmetry. First, the centrosymmetrical crystal is considered. It is supposed that a crystal plate, with certain indices, of the crystal exhibits ferroelectricity. From the supposition, this crystal plate should change from S_1 to S_0 by means of a negative field of a reasonable magnitude. And we notice that the crystal plate is normally nonpolar (see Sec. 5.5). Hence, it is thought that the crystal plate should change from S_1 to some state S_2 (other than S_0 and S_1) by means of a positive field of almost the same magnitude. Thus, the crystal plate should have many like states. When a positive field of magnitude enough to give rise to the state transition is applied to the crystal plate in S_0, the state transition should progress over S_1, as $S_0 \rightarrow S_1 \rightarrow S_2 \rightarrow \cdots$, and eventually the crystal plate should break down. (This process of breakdown is too schematic. In the actual breakdown process, the crystal plate does not step on several states in order as stated above; rather, the concept of "stable states," itself, becomes impossible.) In other words, unless such a strong field as to bring about breakdown is applied, the state transition may not occur. This crystal plate, therefore, cannot be regarded as ferroelectric.

In general, the normally nonpolar crystal plates, even though belonging to the noncentrosymmetrical groups, are not expected to be ferroelectric. A model crystal shown in Fig. 6 may serve as an example. It belongs to $\bar{4}$, one of the noncentrosymmetrical groups. It consists of three kinds of ions, and has no disorder. The first, the second, and the third ion possess electric charges q_1, q_2, and $-q_3$ ($q_1 > 0$, $q_2 > 0$, $q_1 + q_2 = 2q_3$), respectively, and have no dipoles. The fundamental translation vector **c** is parallel to the $\bar{4}$ axis, and **a**, **b**, **c** are normal to each other, and the magnitude of **a** is equal to that of **b**. We use the following type of unit cell: It consists of one first ion existing, in parts, at the eight apexes of the rectangular parallelepiped formed by **a**, **b**, **c**, and one second ion existing at the body center, and two third ions existing, in parts, on the four side faces parallel to **c**, each fraction of the third ions being at a distance **c**/4 or $-$**c**/4 from one of the middle points of the edges normal to **c**. The figure shows the projection of the unit cell (there are extra negative ions written); **b** is normal to the paper face, and **c** is parallel to that and orients from left to right horizontally. Full, hatched, and open circles correspond to positions of first, second, and third ions, respectively. It is supposed that a crystal plate normal to **c** has been made. We consider that the unit cell is (a) in the state S_0 and (b) in S_1. When the crystal plate in S_0 is subjected to a positive field, the negative ions might

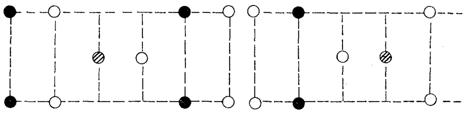
(a) (b)

FIG. 6. Model crystal belonging to the point group $\bar{4}$. The 4 axis is parallel to the paper face and horizontal. The vector **c** is taken as parallel to the $\bar{4}$ axis. Full, hatched, and open circles correspond to positions of positive first, positive second, and negative third ions, respectively. If negative ions in (a) are displaced by $-$**c**/2, (b) is obtained.

move by $-\mathbf{c}/2$ relative to the positive ions, the state transition $S_0 \rightarrow S_1$ resulting; thereafter, when the crystal plate is subjected to a negative field, the negative ions might move by $\mathbf{c}/2$, the state transition $S_1 \rightarrow S_0$ resulting. If so, this crystal plate would be ferroelectric. It is, however, normally nonpolar; therefore when the crystal plate in S_1 is subjected to such a positive field as to give rise to the state transition $S_0 \rightarrow S_1$, the negative ions should move by $-\mathbf{c}/2$, the state transition $S_1 \rightarrow S_2$ resulting (the states S_0 and S_2 are identical in the interior but distinct in the boundaries).

The next problem is whether or not a normally polar crystal plate belonging to one of the noncentrosymmetrical groups except the polar groups can exhibit ferroelectricity. It is supposed that there is a ferroelectric one. We notice that inside the crystal plate in S_1 there is always present a direction-and-sense equivalent to the negative sense of the normal, both making an obtuse angle with one another. The crystal plate in S_1 should therefore change to S_2 by means of a positive field which approximates in magnitude to the negative field giving rise to the state transition $S_1 \rightarrow S_0$. (In the actual process of the state transition, the stage of domain formation may intervene between the initial and final states. This does not affect our reasoning.)

We consider, for illustration, the model crystal plate of Fig. 5 which belongs to one of the noncentrosymmetrical groups except the polar groups. Its main faces are parallel to the plane which goes through the line AB normally to the paper face. We consider that the state in which $f_1 = f$ and $f_2 = 1 - f$ at null field is S_0, and the state in which $f_1 = 1 - f$ and $f_2 = f$ at null field is S_1 ($1/2 < f \leqq 1$; especially at $f = 1$, the crystal has no disorder). When S_0 changes to S_1 by means of a positive field, a positive ion at the first position F, for instance, might move to the second position L; thereafter, when S_1 changes to S_0 by means of a negative field, the positive ion at L might return to F. Inside this crystal, however, three directions parallel to $\overrightarrow{\mathrm{CK}}$, $\overrightarrow{\mathrm{CL}}$, and $\overrightarrow{\mathrm{CN}}$ are equivalent to each other. Therefore, when S_1 is subjected to a positive field, S_1 might change to S_2 in such a way that a positive ion at K, for instance, moves to F or G. Thus, when S_0 is subjected to a positive field, the state transition might progress over S_1, the breakdown resulting.

From the above considerations, it is seen that a crystal plate or a crystal belonging to a nonpolar group is scarcely expected to exhibit ferroelectricity. In fact, the ferroelectric crystals known up to now all belong to the polar groups. But we cannot also conclude that every ferroelectric crystal or crystal plate should belong to a polar group.

6.3. Spontaneous Polarization of the Ferroelectric Crystal Plate

We denote the parameters of the ferroelectric crystal plate by the symbols with and without the superscript #, in the states S_0 and S_1, respectively. At present, S_0 and S_1 refer to null field and null stress. It is supposed that the crystal plate has changed from S_1 to S_0 by means of a negative field. An orderly and stationary *s-g* set is selected. (When $g^{\#}_{ij} = g_{ij}$ for all i and j, or more generally, $g^{\#}_{ij} - g_{ij}$ is independent of i and j, the set of g_{ij} or the set of $g^{\#}_{ij}$ is stationary.) It may be obvious that

$$\left.\begin{array}{c} v^{\#} = v, \quad d^{\#} = d, \\ k^{\#}_{ij} - k_i \quad \text{and} \quad k'^{\#}_{ij} - k'_i \text{ : independent of } i,j. \end{array}\right\} \quad (6.1)$$

The equations

$$q^{\#}_i \approx q_i \quad (6.2)$$

and

$$\textstyle\sum_k \theta^{\#}_{ijk} \approx \Theta_i \quad (6.3)$$

may hold. Therefore,

$$P^{\#}_f \approx P_f \approx \frac{1}{v}\left\{\sum_i q_i \left(\frac{k_i + k'_i}{2}\right) d + \sum_i q_i g_i + \sum_i \Theta_i q_i d\right\}, \quad (6.4)$$

and

$$P - P^{\#} \approx P_v - P^{\#}_v . \quad (6.5)$$

It is evident that $P - P^{\#}$ is independent of boundaries as well as r.s. It may be reasonable to designate $(P - P^{\#})/2$ as the s.p. of the crystal plate (species) in S_1. Spontaneous polarization of this nature is significant solely for the ferroelectric crystal plates.

6.4. Regular Ferroelectric Crystals

There may be a crystal as mentioned below. It has, at null field and null stress, the two stable states S and $S^{\#}$ of which the space lattices are parallel to one another (see Sec. 2.3); a crystal plate, with arbitrary indices, of it alternates between S and $S^{\#}$ by means of suitable electric field alternating, the parallelism of the space lattices being kept (not in the intermediate stage of the state transition, but in S and $S^{\#}$). Such a crystal is provisionally referred to as a "regular ferroelectric crystal." The parameters of a regular ferroelectric crystal are denoted by symbols without and with # in S and $S^{\#}$, respectively. The model crystal shown in Fig. 7 is an example of regular ferroelectric crystal. (It has no disorder and its ions

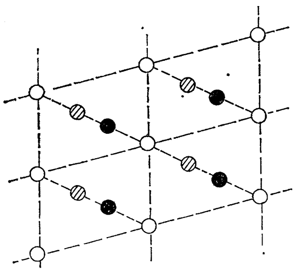

FIG. 7. Regular ferroelectric model crystal. Open circles correspond to positions of negative ions. Positive ions are situated at full circles in S, and at hatched circles in $S^{\#}$.

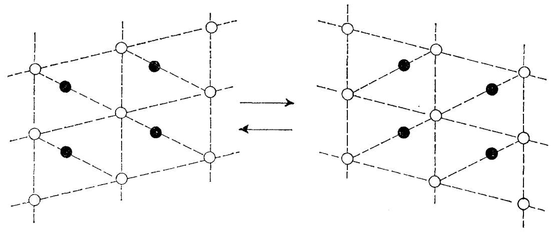

FIG. 8. Irregular ferroelectric model crystal. The electrodes are parallel to the paper face, or are normal to both the paper face and the horizontal plane.

have no dipoles.) It is considered that all positive ions exist at full circles in S and at hatched circles in $S^{\#}$. (The space lattice in S is parallel to that in $S^{\#}$.) The model crystal shown in Fig. 8 is an example of an irregular ferroelectric crystal. The electrodes are, for instance, parallel to the paper face, or are normal to both the paper face and the horizontal plane. The crystal structure in one state is the same as that in the other, but the space lattice in one state is not parallel to that in the other. Among actual ferroelectric crystals, sodium nitrite is thought regular, and Rochelle salt is irregular; the crystal plate normal to the polar axis of the latter crystal has the space lattices not parallel in both states.

It is to be noted that the state alternation $S \rightleftharpoons S^{\#}$ within the definition of regularity means the reversibility $\mathbf{s}_{ij} \rightleftharpoons \mathbf{s}_{ij}^{\#}$. In relation to this, the consideration below may be informative. The model crystal of Fig. 5 is taken up. We consider that the state where $f_1 = 0$ and $f_2 = 1$ is S and the state where $f_1 = 1$ and $f_2 = 0$ is $S^{\#}$. Now, the positive ion at M is watched. When $S \rightarrow S^{\#}$, the ion is supposed to move to F. When thereafter $S^{\#} \rightarrow S$, the ion will move to K, L, or M with an equal probability; it does not necessarily return to M. (If the ion should reciprocate between F and M by means of a suitable alternating field parallel to the line FM, then it would reciprocate between F and L by means of a field parallel to the line FL.) Thus, the reversibility $\mathbf{s}_{ij} \rightleftharpoons \mathbf{s}_{ij}^{\#}$ is not satisfied; but, viewing the interior alone and not the boundaries of the crystal, the state alternation $S \rightleftharpoons S^{\#}$ appears as if it were realized.

We consider the polarization of the regular ferroelectric crystal. An orderly and stationary **s-g** set is selected. For an arbitrary sample of a crystal plate, with arbitrary indices, of the crystal, the equations

$$q_i^{\#} \approx q_i, \quad \sum_k \theta_{ijk}^{\#} \approx \Theta_i \tag{6.6}$$

may hold. It may be obvious that

$$\left.\begin{array}{r} v^{\#} = v, \quad d^{\#} = d, \\ k_{ij}{}^{\#} - k_i \quad \text{and} \quad k_{ij}'^{\#} - k_i' : \text{independent of } i,j. \end{array}\right\} \tag{6.7}$$

Therefore, we obtain

$$\left.\begin{array}{l} \mathbf{P}_v = (1/v)\{ \sum_{i,j} f_{ij} q_{ij} (\mathbf{s}_{ij} - \mathbf{g}_i) + \sum_{i,j} f_{ij} \mathbf{p}_{ij} \} , \\ \mathbf{P}_v^{\#} = (1/v)\{ \sum_{i,j} f_{ij}^{\#} q_{ij}^{\#} (\mathbf{s}_{ij}^{\#} - \mathbf{g}_i) + \sum_{i,j} f_{ij}^{\#} \mathbf{p}_{ij}^{\#} \} , \end{array}\right\} \tag{6.8}$$

and

$$P_f^{\#} \approx P_f, \quad P - P^{\#} \approx \mathbf{n} \cdot (\mathbf{P}_v - \mathbf{P}_v^{\#}) . \tag{6.9}$$

From (6.9), it is evident that $P - P^{\#}$ is independent of boundaries as well as r.s., and moreover, that there exists a vector $\mathbf{P}_s$ which satisfies

$$P - P^{\#} \approx 2\mathbf{n} \cdot \mathbf{P}_s , \tag{6.10}$$

and which is independent of r.s., crystal-plate orientation, and crystal-plate boundaries. When an orderly and stationary r.s. is selected, the equation

$$\mathbf{P}_s = (\mathbf{P}_v - \mathbf{P}_v^{\#})/2 \tag{6.11}$$

is valid. $\mathbf{P}_s$ is thought to be characteristic of both S and $S^{\#}$, and therefore the regular ferroelectric crystal must be polar (see Sec. 5.1). In a regular ferroelectric crystal belonging to one of the polar groups except 1 and m, the polar axes in both states must be parallel to $\mathbf{P}_s$ and hence to one another. It may be reasonable to designate $\mathbf{P}_s$ and $\mathbf{P}_s^{\#} = -\mathbf{P}_s$ as the s.p.v.'s of the crystal in S and $S^{\#}$, respectively. As to some ferroelectric crystals, their "observed s.p.v.'s" have been reported. It may be noticed that they are of the same nature as that of the s.p.v. defined here. This s.p.v., however, should not be conceived the same as ⟨s.p.v.⟩ (see Sec. 5.1). The former is not *a priori* postulated but defined by (6.10) or (6.11); it is significant solely for the regular ferroelectric crystals; it is not determined by the internal charge configuration in the state, alone, but by the configurations in both states and the connection between these configurations. We have obtained two natures of s.p.v.'s, viz., pyroelectric s.p.v. (see Sec. 5.4) and ferroelectric s.p.v. It should not be conceived that both are of the same nature and therefore of equal value. Both are of different natures. Whether or not both are of equal value is to be examined (see Sec. 6.7).

In the irregular ferroelectric crystal, the space lattices in the two states are not parallel to one another; hence the vector **n** is not so naively defined as before. A crystal plate, with certain indices, of the crystal might be differently thick in the two states. (In the definition of ferroelectricity, we required the same thickness in the two states. This stipulation is important but not indispensable.) As to the irregular ferroelectric crystal, therefore, we do not connect its particular crystal plates (species) with the infinite crystal.

6.5. Types of State Transition of the Regular Ferroelectrics

Since the regular ferroelectric crystal has the same structure in the two states, one state should be obtained by performing upon the other state an operation of the rotation group (and a translation operation); this operation must be such that the space lattice in one state is parallel to that in the other state. When this operation is found, it is possible to find one state from the other, and to know how the crystal constants (tensorial in general) change at the state transition; and it is further possible to classify the regular ferroelectric crystals in accordance with their own operations. In this section these problems are treated.

The elements of the rotation group which keep the general triclinic lattice parallel are the identity operation 1 and the inversion operation $\bar{1}$. In the regular ferroelectric crystal belonging to the point group 1, therefore, one of the two states is considered to be obtained by performing the inversion upon the other. (This does not mean that all ions are actually inverted through a fixed point in the process of the state transition.) The crystal constants undergo the inversion at the state transition; for instance, vectorial constants have (only) their sense changed, and tensors of rank two do not undergo any change. Hence the s.p.v. has (only) its sense changed; this is consistent with the definition of the s.p.v. in Sec. 6.4.

The elements of the rotation group which keep the general monoclinic lattice parallel are $1,\bar{1},2$, and m; 2 means the 180° rotation about the monoclinic unique axis, and m means the reflection across a plane normal to the monoclinic unique axis. We first consider the regular ferroelectric crystal belonging to the point group m. While the operation m does not affect the crystal, the remaining operations $\bar{1}$ and 2 have the same effect on it. One of the two states is therefore considered to be obtained by performing $\bar{1}$ or 2 upon the other. At the state transition, vectorial constants have (only) their sense changed, since they are normal to the monoclinic unique axis. We next consider the regular ferroelectric crystal belonging to the point group 2. While 2 does not affect the crystal, the remaining operations $\bar{1}$ and m have the same effect on it. One of the two states is therefore considered to be obtained by performing $\bar{1}$ or m upon the other. At the state transition, vectorial constants have (only) their sense changed, since they are parallel to the monoclinic unique axis. Triglycine sulfate is thought of as an example.

The elements of the rotation group which keep the general orthorhombic lattice parallel are

$$1,\bar{1},2_x,2_y,2_z,m_x,m_y, \text{ and } m_z;$$

x, y, and z are the three orthorhombic axes; 2_x means the 180° rotation about the x axis, and m_x means the reflection across a plane normal to the x axis. The regular ferroelectric crystal belonging to the point group $mm2$ has the orthorhombic lattice. If z is its polar axis, then $1,2_z,m_x$, and m_y do not affect it; while $\bar{1},2_x,2_y$, and m_z have the same effect on it. One of the two states is therefore considered to be obtained by performing m_z upon the other. Sodium nitrite is thought of as an example.

The elements of the rotation group which keep the general tetragonal lattice parallel are

$$1,\bar{1},2_1,2_2,2_3,2_4,m_1,m_2,m_3,m_4,2,m,4,4^3,\bar{4}, \text{ and } \bar{4}^3;$$

$4,4^3,\bar{4}$, and $\bar{4}^3$ mean the 90° rotation, the 270° rotation, the 90° rotatory inversion, and the 270° rotatory inversion about the tetragonal unique axis, respectively; 2 means the 180° rotation about the tetragonal unique axis, and m means the reflection across a plane normal to the tetragonal unique axis; m_1 means the reflection across a plane parallel to one of the side faces of the tetragonal prism, and m_n means the reflection across the plane resulting from an $(n - 1) \times 45°$ rotation of the m_1 plane about the tetragonal unique axis, and 2_n means the 180° rotation about an axis normal to the m_n plane. In the regular ferroelectric crystal belonging to the point group 4 or $4mm$, only $\bar{1},2_n,m,\bar{4}$, and $\bar{4}^3$ change the sense of the s.p.v. In one belonging to $4mm$, these all have the same effect; one of the two states is therefore obtained by performing m upon the other. In one belonging to 4, operations $\bar{1},m,\bar{4}$, and $\bar{4}^3$ have the same effect, operations $2_1,2_2,2_3$, and 2_4 have the same effect, while m and 2_n have different effects. Therefore, two kinds are conceivable: In the crystal of the first kind, one of the two states is obtained by performing m upon the other, and in the second kind, one state is obtained by performing 2_1 or 2_2 upon the other. Vectorial constants are parallel to the polar axis; at the state transition they have (only) their sense changed, in either kind. When the z axis is the polar axis, and the x and y axes are normal to one another and to the z axis, a tensorial constant of rank two is generally represented by

$$\begin{pmatrix} \alpha & \gamma & 0 \\ -\gamma & \alpha & 0 \\ 0 & 0 & \beta \end{pmatrix}$$

(α, β, γ are free from any rotation of the x and y axes about the z axis). In the first kind, this tensor does not vary at the state transition, but in the second kind, it varies to

$$\begin{pmatrix} \alpha & -\gamma & 0 \\ \gamma & \alpha & 0 \\ 0 & 0 & \beta \end{pmatrix}$$

(the x, y, and z axes are spatially fixed).

As is well known, in the trigonal system there are two types of lattice, viz., trigonal R lattice and hexagonal P lattice. In the hexagonal system there is only one type of lattice, hexagonal P. First, the trigonal R lattice is considered. The elements of the rotation group which keep the lattice parallel are

$$1, \bar{1}, 2, 2', 2'', m, m', m'', 3, 3^2, \bar{3}, \text{ and } \bar{3}^2;$$

$3, 3^2, \bar{3}$, and $\bar{3}^2$ mean the 120° rotation, the 240° rotation, the 120° rotatory inversion, and the 240° rotatory inversion about the trigonal unique axis, respectively; m means the reflection across a plane parallel to both the trigonal unique axis and one of the edges of the rhombohedron (m' and m'' are similar), and 2 means the 180° rotation about an axis normal to the m plane ($2'$ and $2''$ are similar). In the regular ferroelectric crystal belonging to the point group 3 or $3m$, merely $\bar{1}, 2, 2', 2''$, $\bar{3}$, and $\bar{3}^2$ change the sense of the s.p.v. In one belonging to $3m$, these all have the same effect; one of the two states is therefore considered to be obtained by performing the inversion upon the other. Potassium nitrate(ferroelectric) may be thought of as an example. In the present case, the reflection across a plane normal to the polar axis does not keep the lattice parallel. In one belonging to 3, operations $\bar{1}, \bar{3}$, $\bar{3}^2$ have the same effect, and operations $2, 2', 2''$ have the same effect, while $\bar{1}$ and 2 have different effects. Hence, two kinds are conceivable: In the first kind, one of the two states is obtained by performing the inversion upon the other, and in the second kind, one state is obtained by performing 2 upon the other. (The operation 2 is equivalent to the inversion followed by the reflection m.)

The elements of the rotation group which keep the hexagonal P lattice parallel are

$$1, \bar{1}, 2_n, m_n, 2, m, 6^n, \text{ and } \bar{6}^n \ (n = 1, 2, \cdots, 6);$$

6^n and $\bar{6}^n$ mean the $n \times 60°$ rotation and the $n \times 60°$ rotatory inversion about the hexagonal unique axis, respectively; 2 means the 180° rotation about the hexagonal unique axis, and m means the reflection across a plane normal to the hexagonal unique axis; m_1 means the reflection across a plane parallel to one of the side faces of the hexagonal prism, and m_n means the reflection across the plane resulting from an $(n - 1) \times 30°$ rotation of the m_1 plane about the hexagonal unique axis, and 2_n means the 180° rotation about an axis normal to the m_n plane. It may be noticed that 6^6 and 1, $\bar{6}^6$ and $\bar{1}$, 6^3 and 2, and $\bar{6}^3$ and m have the same effect, respectively. In the regular ferroelectric crystal belonging to the point group 3, $3m$, 6, or $6mm$, merely $\bar{1}, 2_n, m$, and $\bar{6}^n$ change the sense of the s.p.v. In one belonging to $3m$, operations $\bar{1}$ and m have different effects, and each of the rest has the same effect as that of either $\bar{1}$ or m. Consequently, two kinds are conceivable; in the first kind, one of the two states is obtained by performing the inversion upon the other, and in the second kind, one state is obtained by performing m upon the other.

In the crystal belonging to the point group 3, operations $\bar{1}, \bar{6}^2, \bar{6}^4$ have the same effect, operations $m, \bar{6}, \bar{6}^5$; $2_1, 2_3, 2_5$; and $2_2, 2_4$, 2_6 have the same effect, respectively, while any two of $\bar{1}, m, 2_1$, and 2_2 have different effects. Consequently, four kinds are conceivable; in the first, second, third, or fourth kind, one of the two states is obtained by performing $\bar{1}, m, 2_1$, or 2_2 upon the other. We now take the z axis as parallel to the polar axis, and the x axis as parallel to the 2_1 axis, and the y axis in such a way that the x, y, and z axes make a right-handed Cartesian coordinate system. Then a tensorial constant of rank two is generally represented by

$$\begin{pmatrix} \alpha & \gamma & 0 \\ -\gamma & \alpha & 0 \\ 0 & 0 & \beta \end{pmatrix}$$

In the first and second kinds, this tensor does not vary at the state transition, but in the third and fourth kinds, it varies to

$$\begin{pmatrix} \alpha & -\gamma & 0 \\ \gamma & \alpha & 0 \\ 0 & 0 & \beta \end{pmatrix}$$

A tensorial constant of rank three, t_{ijk} ($t_{ijk} = t_{ikj}$), is generally represented by

$$\begin{pmatrix} a & -b & e \\ & -a & f \\ & & 0 \end{pmatrix} \quad \begin{pmatrix} -b & -a & -f \\ & b & e \\ & & 0 \end{pmatrix} \quad \begin{pmatrix} d & 0 & 0 \\ & d & 0 \\ & & c \end{pmatrix}$$

where the first, second, and third matrices correspond to matrices (t_{1jk}), (t_{2jk}), and (t_{3jk}), respectively. At the state transition, this tensor varies, in the first kind, to

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

in the second kind, to

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

in the third kind, to

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

and in the fourth kind, to

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

As to a tensor of rank one, i.e., a vector, there is no distinction among all the kinds; on a tensor of rank two, there is no distinction between the first and second kinds, nor between the third and fourth kinds, but the former kinds are distinct from the latter ones; on a tensor of rank three, any two kinds are distinct from one another.

In the crystals belonging to $6mm$, all the operations $\bar{1}, 2_n, m$, and $\bar{6}^n$ are of the same effect, so that there is only one kind. In the crystals belonging to the point group 6, operations $\bar{1}, m, \bar{6}^n$ are of the same effect, and operations $2_1, 2_2, \cdots, 2_6$ are so, while m and 2_n have different effects. Consequently, the crystals are classified into two kinds.

From the above consideration, it is evident that one of the two states of a regular ferroelectric crystal is obtained by performing upon the other the inversion or the reflection across a plane normal to the s.p.v. or the 180° rotation about an axis normal to the s.p.v. The first, second, and third types are provisionally referred to as "inversion type," "reflection type," and "rotation type," respectively. The reflection type appears in every point group, but the reflection type and the rotation type do not. In some point groups, there is no distinction among the three types, and in some other point groups, there is no distinction between two types while the rest is distinct from the two. In some point groups there are two different rotation types, according to different orientations in the rotation axis. Table I shows the classification of the regular ferroelectric crystals according to their point groups and their types of state transition.

6.6. One-Dimensional Regularity of the Ferroelectric Crystal Plates

We first consider the one-dimensional crystal exhibiting ferroelectricity. All the elements of the one-dimensional rotation group are the identity operation and the inversion operation. A tensor in the one-dimensional space is either of rank zero or of rank one, i.e., a scalar or else a vector; the inversion operation does not affect the former but does change the sign (alone) of the latter. It may be obvious that if a one-dimensional crystal is ferroelectric, it is regular, one of its two states being obtained by performing the inversion upon the other. At the state transition, therefore, scalar constants do not undergo any change, while vectorial constants have their sign changed.

We next consider the correspondence of a crystal plate to a one-dimensional crystal. When a crystal plate having parameters s_{ij}, etc., is present, then corresponding to it, a one-dimensional crystal having the same parameters (except v) is imaginable. It is thought that the one-dimensional crystal corresponding to a ferroelectric crystal plate (species) is also ferroelectric, and that a constant of the latter is also a constant of the former. At the state transition, therefore, a constant of the ferroelectric crystal plate (species) may either remain unchanged (when scalar)

TABLE I. State-transition types of regular ferroelectrics.

System	Point group	Number of kinds	Type of state transition
Triclinic	1	1	Inversion
Monoclinic	m	1	Inversion, Rotation
	2	1	Inversion, Reflection
Orthorhombic	$mm2$	1	Inversion, Reflection, Rotation
Tetragonal	4	2	(I) Inversion, Reflection (II) Rotation
	$4mm$	1	Inversion, Reflection, Rotation
Trigonal	3 (Tri. R)	2	(I) Inversion (II) Rotation
	$3m$ (Tri. R)	1	Inversion, Rotation
	3 (Hex. P)	4	(I) Inversion (II) Reflection (III) Rotation (IV) Rotation
	$3m$ (Hex. P)	2	(I) Inversion, Rotation (II) Reflection, Rotation
Hexagonal	6	2	(I) Inversion, Reflection (II) Rotation
	$6mm$	1	Inversion, Reflection, Rotation

or have its sign changed (when vectorial). Such "one-dimensional regularity" of the ferroelectric crystal plate is important. The s.p. defined in Sec. 6.3 had only its sign changed at the state transition; this does result also from the one-dimensional regularity. In the definition of ferroelectricity in Sec. 6.1, we required the invariability of the thickness of the crystal plate at the state transition; this is just consistent with the invariability of the total length of the ferroelectric one-dimensional crystal at the state transition. (In the two states, the ferroelectric one-dimensional crystal has the same structure and therefore the same total length. Thus, the latter follows from the former and is no independent requirement.)

6.7. Relationship between the Pyroelectric and the Ferroelectric Spontaneous Polarization

In Sec. 6.4, the s.p.v. of the regular ferroelectric crystal was defined at null stress, but it is also possible to think of the s.p.v. at a strain σ. (This does not mean that the crystal is being kept at the strain σ through the process of state transition. We are now thinking of two states stable at the strain σ.) The regular ferroelectric crystal having a phase transition to a nonpolar phase at a temperature $T_t(\sigma)$ under constant strain σ and null field possesses the pyroelectric s.p.v. and the ferroelectric s.p.v., temporarily denoted by $\mathbf{P}_s^p$ and $\mathbf{P}_s^f$, respectively. We investigate whether they agree with one another in value (though they have different natures). We select such an orderly and stationary r.s. as gives zero bk.p.v. in the nonpolar phase. From (5.9), we have

$$\mathbf{P}_s^p = \mathbf{P}_v \quad \text{and} \quad \mathbf{P}_s^{p\#} = \mathbf{P}_v^{\#} \tag{6.12}$$

for the two states S and $S^{\#}$, respectively. (On this occasion it has been assumed that the two states S and $S^{\#}$ become the same in the nonpolar phase.) Now, the equation

$$\mathbf{P}_s^{p\#} = -\mathbf{P}_s^p \tag{6.13}$$

must hold; for, if the regular ferroelectric crystal belongs to the point group 1 or m, it is of inversion type, or if it belongs to one of the polar groups except 1 and m, the pyroelectric s.p.v. is parallel to the polar axis. From Eqs. (6.11), (6.12), and (6.13), it follows that

$$\mathbf{P}_s^f = \mathbf{P}_v \, . \tag{6.14}$$

From this and (6.12), the equation

$$\mathbf{P}_s^p = \mathbf{P}_s^f \tag{6.15}$$

results. Thus, it has been verified that $\mathbf{P}_s^p$ and $\mathbf{P}_s^f$ are equal in value, and incidentally that (6.14) is valid if we select such an orderly and stationary r.s. as gives zero bk.p.v. in the nonpolar phase. In (6.14) and (6.15), σ can of course be the strain at null stress.

We next examine, on the crystal plate, whether its pyroelectric s.p. P_s^p and ferroelectric s.p. P_s^f at null stress agree with one another in value. This crystal plate is to change from a phase α to a phase β at a temperature T_t under null stress and null field, it being ferroelectric in α and normally nonpolar in β. It is assumed that the two states S and $S^{\#}$ in α become identical in β. If we select an orderly and stationary r.s. giving zero bk.p. in β, we obtain, from (5.11),

$$P_s^p = P_v \quad \text{and} \quad P_s^{p\#} = P_v^{\#} \tag{6.16}$$

for S and $S^{\#}$, respectively. Because of the one-dimensional regularity (see Sec. 6.6),

$$P_s^{p\#} = -P_s^p \, . \tag{6.17}$$

From (6.16), (6.17), and Sec. 6.3, it follows that

$$P_s^f = P_v \, . \tag{6.18}$$

From this and (6.16), the equation

$$P_s^p = P_s^f \tag{6.19}$$

results. Thus, it has been found that at null stress also, the pyroelectric s.p. and the ferroelectric s.p. are equal in value.

6.8. Pyroelectricity of Ferroelectric Crystals

First, the pyroelectricity of the regular ferroelectric crystal is investigated; the crystal need not have a phase transition to a nonpolar phase. An orderly and stationary r.s. is selected. Since $\partial\mathbf{P}_v/\partial T$ at constant strain is a crystal constant (see Sec. 3.4), it is evident that

$$\partial(\mathbf{P}_v^{\#})/\partial T = (\partial\mathbf{P}_v/\partial T)^{\#} = -\partial\mathbf{P}_v/\partial T \, . \tag{6.2\ }$$

From this and (6.11), it follows that

$$\partial\mathbf{P}_s^f/\partial T = \partial\mathbf{P}_v/\partial T \, . \tag{6.21}$$

From this and (3.13), the equation

$$\partial\mathbf{P}_s^f/\partial T = \boldsymbol{\pi} \tag{6.22}$$

results. The (nonzero) ferroelectric s.p.v. may in general vary with temperature, so that the regular ferroelectric crystal is generally expected to be pyroelectric.

We next examine the pyroelectricity of the ferroelectric crystal plate which need not become normally nonpolar at a temperature. At null stress we have

$$\partial P_s^f/\partial T = \tfrac{1}{2}\{\partial P/\partial T - (\partial P/\partial T)^{\#}\} \, , \tag{6.23}$$

from Sec. 6.3. Since the pyroelectric coefficient

$\partial P/\partial T$ is ordinarily a constant of the crystal plate (see Sec. 4.3), the equation

$$(\partial P/\partial T)^{\#} \approx -\partial P/\partial T \tag{6.24}$$

may ordinarily hold, from one-dimensional regularity. Substituting this into (6.23), we eventually obtain

$$\partial P_s^f/\partial T \approx \partial P/\partial T\,. \tag{6.25}$$

The (nonzero) ferroelectric s.p. may, in general, vary with temperature, so that the ferroelectric crystal plate may, in general, be pyroelectric.

6.9. Excepted Regular Ferroelectrics

In Sec. 6.5, the lattice of a regular ferroelectric crystal belonging to the point group 1, for instance, was assumed to be a general parallelepiped, and no reference was made to the case that the lattice is a rectangular parallelepiped. This special case is now considered. The elements of the rotation group which keep a general rectangular parallelepiped parallel are

$$1,\bar{1},2_x,2_y,2_z,m_x,m_y,\ \text{and}\ m_z$$

(see Sec. 6.5). Any two of them have different effects on the crystal, so that seven kinds are conceivable. In Sec. 6.5, only the $\bar{1}$ type was taken into account; hence the other six types are new. The s.p.v. (ferroelectric) has only its sense changed at the state transition, so that the orientation of the s.p.v., though being arbitrary in the $\bar{1}$ type, is limited in the other types; for instance, in the 2_x type, the s.p.v. must be normal to the x axis, and in the m_x type, it must be parallel to the x axis.

On the 2_x (or m_x) type, for instance, we examine whether the pyroelectric s.p.v. and the ferroelectric s.p.v. are equal or not. Equation (6.12) is valid in this case also. Equation (6.13) might, however, be invalid since $\mathbf{P}_s^p$ might not be normal (or parallel) to the x axis. Consequently, the validity of (6.14) and (6.15) is not assured. In general,

$$\mathbf{P}_s^f = \tfrac{1}{2}\,(\mathbf{P}_s^p - \mathbf{P}_s^{p\#})\,.$$

As to the relation between $\partial \mathbf{P}_s^f/\partial T$ and $\boldsymbol{\pi}$, Eqs. (6.21) and (6.22) might be invalid since (6.20) might not hold. In general,

$$\partial \mathbf{P}_s^f/\partial T = \tfrac{1}{2}\,(\boldsymbol{\pi} - \boldsymbol{\pi}^{\#})\,.$$

In Sec. 6.5, we took no account of those regular ferroelectric crystals of which the lattice belongs to a different system (of crystal symmetry) from that of their substance, as above exemplified. It was except for these crystals that the equalities between the pyroelectric and ferroelectric s.p.v.'s and between $\partial \mathbf{P}_s^f/\partial T$ and $\boldsymbol{\pi}$ were verified in Secs. 6.7 and 6.8, respectively. For these crystals, such equalities are not assured. However, it is a question whether they exist really. At null stress, it is thought quite accidental that (for instance) the substance is triclinic while the lattice is orthorhombic. Even though the lattice happens to be orthorhombic at one temperature, it may become triclinic if temperature is changed. Hence, it is thought that there are no regular ferroelectric crystals except those considered in Sec. 6.5.

7. SUMMARY

(Sections 2.1 to 2.8)

(1) The polarization of a crystal plate consists of the component of the "bulk polarization vector" in the normal direction (i.e., the "bulk polarization") and the "boundary polarization."

(2) The concept of "reference structure" is introduced.

(3) Polarization of a crystal plate is dependent upon boundaries and independent of reference structure. Bulk polarization vector is dependent upon reference structure and independent of boundaries. Boundary polarization is dependent upon both reference structure and boundaries.

(4) Except in case boundary polarization is negligibly small compared with bulk polarization, it should not be conceived that polarization is equal to bulk polarization.

(5) The concept of "orderly reference structure" is introduced. In the crystals without disorder, any reference structure is orderly.

(Sections 3.1 to 3.6)

(1) The concept of "stationary reference structure" is introduced.

(2) A crystal which transforms its phase at a certain temperature under constant strain and null field possesses "polarization difference vector due to the phase transition," $\boldsymbol{\Pi}$, as a crystal constant independent of reference structure, crystal-plate orientation, and crystal-plate boundaries. As to a crystal plate, with arbitrary indices, of this crystal, its polarization difference due to the phase transition is equal to the normal component of $\boldsymbol{\Pi}$. If an orderly and stationary reference structure is selected, $\boldsymbol{\Pi}$ is equal to the difference between the bulk polarization vectors in the two phases.

(3) The crystal exhibiting pyroelectricity at constant strain possesses "pyroelectric vector" $\boldsymbol{\pi}$ as a crystal constant independent of reference structure, crystal-plate orientation, and crystal-plate bounda-

ries. Pyroelectric coefficient of a crystal plate, with arbitrary indices, of this crystal is equal to the normal component of $\boldsymbol{\pi}$. If an orderly and stationary reference structure is selected, the equation $\boldsymbol{\pi} = \partial \mathbf{P}_v / \partial T$ holds (where $\mathbf{P}_v$ is bulk polarization vector and T is temperature).

(4) A crystal has "susceptibility tensor" $\tilde{\chi}$ at constant strain as a crystal constant independent of reference structure, crystal plate orientation, and crystal-plate boundaries. Susceptibility at constant strain of a crystal plate, with arbitrary indices, of this crystal is equal to $\mathbf{n}\tilde{\chi}\mathbf{n}$ (where $\mathbf{n}$ is the normal vector of the crystal plate). If an orderly and stationary reference structure is selected, the equation $[\tilde{\chi}]_{ij} = (1/2)\,(\partial P_{vi}/\partial E_j + \partial P_{vj}/\partial E_i)$ is valid, where E_i and P_{vi} are the i component ($i = x,y,z$) of electric field $\mathbf{E}$ and bulk polarization vector $\mathbf{P}_v$, respectively).

(Sections 4.1 to 4.4)

(1) With respect to the crystal plate at null stress also, it is convenient to employ the concepts of "reference structure," "orderly reference structure," and "stationary reference structure."

(2) An ordinary crystal plate (species) possesses, at null stress, pyroelectric coefficient π and susceptibility χ as its constants.

(3) At null stress, there are not generally present the crystal constants $\boldsymbol{\pi}$ and $\tilde{\chi}$ satisfying the equations $\pi = \mathbf{n}\cdot\boldsymbol{\pi}$ and $\tilde{\chi} = \mathbf{n}\tilde{\chi}\mathbf{n}$ over all possible $\mathbf{n}$.

(Sections 5.1 to 5.5)

(1) It is improper to presuppose the existence of ⟨spontaneous polarization vector⟩ in all the crystals which exhibit pyroelectricity or which belong to the polar groups.

(2) The crystals exhibiting pyroelectricity at constant strain belong to the polar groups (because they possess pyroelectric vector).

(3) It is possible to define pyroelectric "spontaneous polarization vector" for those pyroelectric crystals which have a phase transition to a nonpolar phase at constant strain. If we select such an orderly and stationary reference structure as gives zero bulk polarization vector in the nonpolar phase at the strain, then in the pyroelectric phase, spontaneous polarization vector is equal to bulk polarization vector.

(4) It is possible to define pyroelectric "spontaneous polarization" for those pyroelectric crystal plates (species) which become "normally nonpolar" at a certain temperature under null stress.

(Sections 6.1 to 6.9)

(1) Such a definition of "ferroelectricity" is improper which presupposes the existence of ⟨spontaneous polarization vector⟩. (The definition in this paper is not such.)

(2) A crystal plate or a crystal belonging to a nonpolar group is scarcely expected to exhibit ferroelectricity; but it is not concluded that *every* ferroelectric crystal or crystal plate should belong to a polar group.

(3) It is possible to define ferroelectric "spontaneous polarization" for a ferroelectric crystal plate (species).

(4) It is possible to define ferroelectric "spontaneous polarization vector" for the "regular ferroelectric" crystals. These crystals must belong to the polar groups.

(5) There are three types of state transition of the regular ferroelectrics, viz., "inversion type," "reflection type," and "rotation type." The regular ferroelectrics are divided into nineteen subclasses, according to their point groups and their types of state transition. The change in their crystal constants (generally tensorial) accompanying the state transition is unique in each subclass.

(6) The regular ferroelectric crystal having a phase transition to a nonpolar phase at constant strain possesses two different natures of spontaneous polarization vectors, viz., pyroelectric one and ferroelectric one. They are equal in value to one another.

(7) The ferroelectric crystal plate (species) which becomes normally nonpolar at a certain temperature under null stress possesses pyroelectric spontaneous polarization and ferroelectric spontaneous polarization. These are equal in value though different in nature.

(8) If $\mathbf{P}_s^f$ is the ferroelectric spontaneous polarization vector of a regular ferroelectric crystal (which need not have a phase transition to a nonpolar phase), then the equation $\partial \mathbf{P}_s^f / \partial T = \boldsymbol{\pi}$ (at constant strain) is valid.

(9) If P_s^f is the ferroelectric spontaneous polarization of a ferroelectric crystal plate (which need not become normally nonpolar at a certain temperature), then $\partial P_s^f / \partial T$ (at null stress) is, ordinarily, almost equal to the pyroelectric coefficient at null stress.

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