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Theory of the Degree of the Free-Energy Function for Ferroelectrics

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The free-energy function in the thermodynamical theory of ferroelectrics is often put approximately equal to a *finite* power series in the components of the polarization vector. It is obvious that in general, in order to be able to give an account of ferroelectric phenomena, the free-energy function has to be of fourth degree at the lowest. In this paper, a free-energy function Φ of a certain degree is said to be able to describe a ferroelectric, when Φ permits the ferroelectric (i) to exist as a stable or metastable phase and (ii) to transform to a paraelectric phase. These two stipulations are the minimum condition necessary for any ferroelectric phase to be properly a "ferroelectric phase." The lowest degree necessary for the free-energy function to be able to describe a ferroelectric is referred to, briefly, as the "describability limit" of the ferroelectric. It is anticipated that the describability limits of all the ferroelectrics which belong to one and the same *species* have a *lower limit* (in the mathematical sense) which may not generally be 4. This lower limit is referred to as the describability limit of the species. The describability limit of a ferroelectric may depend on whether it is under zero stress or under constant strain, but the describability limit of a species does not. A determination is made of whether the describability limit of each of the 55 species is 4 or larger. As a result, it is found that 28 species—F$\bar{1}$(1)A1, etc.—are of describability limit 4, and that the describability limits of the other 27 species—F2/*m*(2)A1, etc.—must be larger than 4; they are not all 6.

I. INTRODUCTION

For ferroelectrics, there are 55 possible *species*[1] in all, as distinguished according to the point group of their *prototype*[1,2] and the total number and orientation of the equivalent unique ferroelectric directions. These 55 species are represented by the symbols[1]

F$\bar{1}$(1)A1, F2/*m*(2)A1, F2/*m*(1)A2, F2/*m*(1)D2, F222(1)D2, F*mmm*(4)A1, F*mmm*(2)A*m*, F*mmm*(1)D*m*, F$\bar{4}$(1)D$\bar{4}$, F4/*m*(4)A1, F4/*m*(2)A4, F4/*m*(1)D4, F422(2)D2, F422(1)D4, F$\bar{4}$2*m*(2)D2, F$\bar{4}$2*m*(1)D$\bar{4}$, F4/*mmm*(8)A1, F4/*mmm*(4)A2, F4/*mmm*(4)A4, F4/*mmm*(2)D2, F4/*mmm*(1)D4, F$\bar{3}$(3)A1, F$\bar{3}$(1)D$\bar{3}$, F32(1)D3, F$\bar{3}$*m*(6)A1, F$\bar{3}$*m*(3)A*m*, F$\bar{3}$*m*(3)D*m*, F$\bar{3}$*m*(1)D$\bar{3}$, F$\bar{6}$(1)D$\bar{6}$, F6/*m*(6)A1, F6/*m*(3)A6, F6/*m*(1)D6, F622(3)D2, F622(1)D6, F$\bar{6}$*m*2(1)D$\bar{6}$, F6/*mmm*(12)A1, F6/*mmm*(6)A2, F6/*mmm*(6)A6, F6/*mmm*(3)D2, F6/*mmm*(1)D6, F23(3)D2, F*m*3(12)A1, F*m*3(6)A*m*, F*m*3(4)D3, F*m*3(3)D*m*, F432(6)D2, F432(4)D3, F432(3)D4, F$\bar{4}$3*m*(3)D$\bar{4}$, F*m*3*m*(24)A1, F*m*3*m*(12)A2, F*m*3*m*(12)A4, F*m*3*m*(6)D2, F*m*3*m*(4)D3, F*m*3*m*(3)D4.

Previously,[1,3] when we determined theoretically the orders of *ferro-paraelectric*[4] phase transitions, we laid down the following three postulates as bases of the reasoning. (The previous expressions of these postulates included the phrases "at the Curie temperature" and "in the vicinity of the Curie temperature," but the present expressions do not.)

Postulate A (or the postulate of expansibility): The free energy of the crystal can be expressed as an infinite power series in the components of the polarization vector.

Postulate B (or the postulate of analyticity): The expansion coefficients are analytic functions of temperature (if the coordinate axes are taken in a certain consistent way).

Postulate C (or the postulate of nonmultiple crossing): More than one of those expansion coefficients (or those combinations, such as sums or differences, of expansion coefficients) which are expected, from symmetry considerations, to be nonzero in the prototype do not simultaneously become exactly zero at one and the same temperature. (Postulates III and IV in Ref. 3 can be consolidated into a single more elegant expression—Postulate C.)

Postulate A may be most generally valid.[5] But it is often not very useful for the analysis of real ferroelectrics. Many authors[6] assumed that the free energy could approximately be expressed as a *finite* power series (or a polynomial) in the components of the polarization vector, and succeeded in explaining dielectric behavior of some ferroelectrics. Such a free-energy polynomial, usually, is taken as of fourth or sixth degree. (As is defined in algebra, the degree of a polynomial is the highest of the degrees of all the terms contained in the polynomial.) It is obvious that in general, in order to

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[1] K. Aizu, Phys. Rev. **146**, 423 (1966).

[2] K. Aizu, J. Phys. Soc. Japan **21**, 1240 (1966).

[3] K. Aizu, Phys. Rev. **140**, A590 (1965).

[4] As in previous papers, we shall often refer to a transition between a ferroelectric and a paraelectric phase as, briefly, a *ferro-paraelectric* phase transition, and to a transition between a ferroelectric and another ferroelectric phase as, briefly, a *ferro-ferroelectric* phase transition. The phrases "a ferroelectric phase transition of a paraelectric," "a paraelectric phase transition of a ferroelectric," and "a ferro-paraelectric phase transition" mean the same thing, and differ only with respect to the direction of the investigator's view.

[5] Use of the method of the free-energy function in the study of a ferroelectric amounts, automatically, to assuming that the paraelectric phase transformation of the ferroelectric should be *primitive* or *complex in the narrower sense*, whether the free-energy function is expansible in a power series or not. See K. Aizu, J. Phys. Soc. Japan **21**, 2154 (1966).

[6] For instance, A. F. Devonshire, Phil. Mag. **40**, 1040 (1949).

be able to give an account of ferroelectric phenomena, the free energy has to be of fourth degree at the lowest.

In atomic theories of ferroelectrics, the potential energy responsible for the short-range forces among the atoms is, usually, approximated by a finite power series in the deviations of the atoms from their equilibrium positions. The degree of this potential-energy polynomial has a close connection with the degree of the free-energy polynomial in the thermodynamical theory. Therefore, a consideration of the degree of the free-energy function may give a useful suggestion for the atomic theories.

In the present paper, we investigate which of the 55 species of ferroelectrics can and which cannot be described by the free-energy function of fourth degree. Here, the meaning of describability is as follows: A free-energy function Φ of a certain degree is said to be able to describe a ferroelectric, when Φ permits the ferroelectric (i) to exist as a stable or metastable phase and (ii) to transform to a paraelectric phase. (A full account of describability will be given in Sec. II.) These two stipulations are the minimum condition necessary for any ferroelectric phase to be properly a "ferroelectric phase." Thus, when we say that a free-energy function can describe a ferroelectric, we do not mean that the free-energy function can, in a good approximation, explain all characteristic behaviors of the ferroelectric.

The second stipulation might be considered to conflict with the fact that some ferroelectrics exhibit no corresponding paraelectric phases. We, however, regard those ferroelectric as, in themselves, having paraelectric phases, and we imagine that they decompose before reaching the Curie temperature for some reasons which have no direct connection with ferroelectricity.

The lowest degree necessary for the free-energy function to be able to describe a ferroelectric will be referred to, briefly, as the "describability limit" of the ferroelectric. It is obvious that the describability limit of every ferroelectric is an even number not smaller than 4. When one undertakes to carry out an approximate calculation by the method of the free-energy function for a ferroelectric, one must first of all estimate the describability limit of the ferroelectric. We anticipate that the whole of the describability limits of all the ferroelectrics which belong to one and the same species has a *lower limit* (in the mathematical sense) which may not generally be 4. We refer to this lower limit as the describability limit of the species. Then, we may also say that our principal work in this paper is to determine whether the describability limit of each of the 55 species is 4 or larger.

We consider the mechanical conditions. In the present theory, the crystal can be either under zero stress or under constant strain. By "constant strain" we mean that the crystal is in the same state of strain as its prototype. The describability limit of a species is concerned with the form of the free-energy polynomial, but not with the values of the (nonzero) coefficients. In contrast, the describability limit of a particular ferroelectric is concerned with the latter. The form of the free-energy polynomial is independent of whether the crystal is under zero stress or under constant strain (since it is determined by the symmetry of the prototype), but the values of the coefficients are not. Therefore, it turns out that while the describability limit of a species is independent of mechanical conditions, the describability limit of a particular ferroelectric is not. It may sometimes happen that a ferroelectric is impossible under constant strain, though possible under zero stress. In this case, the describability limit under constant strain is absent.

In Sec. III, we consider six species—F$m3m$(12)A4, F$m3m$(6)D2, F23(3)D2, Fmmm(2)Am, F$\bar{3}m$(3)Dm, and F2/m(1)A2—for illustration of the theory. The arguments about the other species are similar and so omitted. All the results are shown in Sec. IV.

II. THE MEANING OF DESCRIBABILITY

That a free-energy function Φ of a certain degree can describe a ferroelectric has the following meaning. Assume that the degree is 4, for example. Φ has the form

$$\Phi=\Phi_0+\sum_{ij} B_{ij}P_iP_j+\sum_{ijk} B_{ijk}P_iP_jP_k +\sum_{ijkl} B_{ijkl}P_iP_jP_kP_l, \quad (1)$$

where P_i ($i=1, 2, 3$, or $=x, y, z$) are the components of the polarization vector $\mathbf{P}$ in the directions of the rectangular coordinate axes x, y, and z, respectively; Φ_0 and B's are functions of the temperature T, which are definite for the ferroelectric. (The first-degree terms $\sum_i B_iP_i$ must be absent. The reason is explained in Ref. 3.) The forms of the tensors B_{ij}, B_{ijk}, and B_{ijkl} must be consistent with the symmetry of the prototype of the ferroelectric. (These tensors are completely symmetric with respect to the indices.)

Φ must increase monotonically with $\|\mathbf{P}\|$ if $\|\mathbf{P}\|$ is large enough. On this account, the sum of all the terms of the highest degree contained in Φ must be positive for any values, not simultaneously zero, of P_x, P_y, P_z:

$$\sum_{ijkl} B_{ijkl}P_iP_jP_kP_l>0 \quad \text{for} \quad \mathbf{P}\neq 0. \quad (2)$$

Φ must give a spontaneous polarization vector. Since the spontaneous polarization vector should be a minimum point of Φ, it must first satisfy the simultaneous equations

$$\partial\Phi/\partial P_i=0 \quad (i=1, 2, 3). \quad (3)$$

It must next satisfy the simultaneous equations that result from replacing P_x, P_y, P_z in the left-hand sides of (3) by $-P_x$, $-P_y$, $-P_z$

$$[\partial\Phi/\partial P_i]_{\mathbf{P}\rightarrow-\mathbf{P}}=0 \quad (i=1, 2, 3) \quad (4)$$

since opposite senses of the spontaneous polarization vector should be completely equivalent to each other. If we use (1) and take the sum and difference between (3) and (4), we can rewrite the whole set of Eqs. (3) and (4) in the form

$$\sum_j B_{ij}P_j+2\sum_{jkl} B_{ijkl}P_jP_kP_l=0 \quad (i=1,\,2,\,3) \tag{5}$$

and

$$\sum_{jk} B_{ijk}P_jP_k=0 \quad (i=1,\,2,\,3). \tag{6}$$

The spontaneous polarization vector must thirdly satisfy the condition

$$\Delta\Phi\equiv\tfrac{1}{2}\sum_{ij}(\partial^2\Phi/\partial P_i\partial P_j)\Delta P_i\Delta P_j>0 \quad \text{for} \quad \Delta\mathbf{P}\neq 0, \tag{7}$$

where $\partial^2\Phi/\partial P_i\partial P_j$ are to be evaluated at the position of the spontaneous polarization vector; the inequality must hold for any values, not simultaneously zero, of ΔP_x, ΔP_y, ΔP_z. Using (1), we have

$$\tfrac{1}{2}\partial^2\Phi/\partial P_i\partial P_j=B_{ij}+3\sum_k B_{ijk}P_k+6\sum_{kl} B_{ijkl}P_kP_l. \tag{8}$$

It can be verified that the condition (7) is always satisfied if $\Delta\mathbf{P}$ is parallel to the spontaneous polarization vector. Put

$$\Delta P_i=aP_i \quad (i=1,\,2,\,3)$$

with a nonzero coefficient a, and substitute these and (8) into the left-hand side of the inequality (7). Then, we have

$$\Delta\Phi=a^2\Big(\sum_{ij} B_{ij}P_iP_j+3\sum_{ijk} B_{ijk}P_iP_jP_k +6\sum_{ijkl} B_{ijkl}P_iP_jP_kP_l\Big).$$

Multiply (5) and (6) by P_i, take the sum with respect to the index i, and substitute the results into the above expression. Then we get

$$\Delta\Phi=4a^2\sum_{ijkl} B_{ijkl}P_iP_jP_kP_l.$$

This is certainly positive, because of the condition (2). Thus, we see that the condition (7) is only significant for $\Delta\mathbf{P}$ perpendicular to the spontaneous polarization vector.

The ferroelectric under consideration should transform to a paraelectric at a certain finite temperature—the Curie temperature T_c. On this account, as T approaches T_c, the difference $\Phi_0-\Phi$ must approach zero. Multiply (5) and (6) by P_i, take the sum with respect to the index i (as we did before), and substitute the results into (1). Then, we get

$$\Phi_0-\Phi=\sum_{ijkl} B_{ijkl}P_iP_jP_kP_l. \tag{9}$$

According to (2), the right-hand side of (9) can become zero only when $\mathbf{P}=0$. Therefore, as T approaches T_c, the spontaneous polarization vector must come to vanish:

$$\mathbf{P}\rightarrow 0 \quad \text{as} \quad T\rightarrow T_c. \tag{10}$$

If Φ satisfies all of the conditions mentioned above, we say that Φ can describe the ferroelectric.

Formula (10) tells that the ferro-paraelectric phase transition must be of second order. This comes from the assumption that Φ is of fourth degree. If Φ is of a higher degree, the condition

$$\Phi_0-\Phi\rightarrow 0 \quad \text{as} \quad T\rightarrow T_c$$

does not lead to (10).

Previously[1,3] we verified that the paraelectric phase transitions of the ferroelectrics of 23 species, F2/*m*(2)A1 etc., are necessarily of first order. From this and the above, one might consider that there is no necessity to investigate anew whether the describability limits of these 23 species are 4 or larger, because it is very obvious that they are larger than 4. This consideration is not, however, quite right.

One reason is as follows. When we determined the orders of ferro-paraelectric phase transitions, we applied the postulate of nonmultiple crossing in a most rigorous way. On the other hand, when we determine the describability limits of ferroelectrics, we use a free-energy function with a finite number of terms, or in other words we assume in the free-energy function that the coefficients in the terms of higher degrees than a certain degree are all zero. This assumption conflicts with the postulate of nonmultiple crossing *in a sense*. Therefore, we need to make a careful investigation of the describability limit even for the 23 species, but expecting that their describability limits will all prove to be larger than 4, and thus no contradiction will arise among conclusions.

Another reason is as follows. The describability limit does not generally have a direct connection with the order of the ferro-paraelectric phase transition. Even though it turns out that the describability limits of the 23 species are larger than 4, the true reason differs from species to species and is not simply because their paraelectric phase transitions are necessarily of first order. This will be seen in Sec. III.

III. ILLUSTRATION OF THE THEORY

1. Species F*m*3*m*(12)A4

We first consider the species F*m*3*m*(12)A4. We take the rectangular coordinate axes x, y, z parallel to the tetrad axes of symmetry of the prototype. We assume that this species can be described by the free-energy function of fourth degree, which has the form

$$\Phi=\Phi_0+B_{11}(P_x^2+P_y^2+P_z^2)+B_{1111}(P_x^4+P_y^4+P_z^4) +6B_{1122}(P_y^2P_z^2+P_z^2P_x^2+P_x^2P_y^2). \tag{11}$$

A necessary and sufficient condition for (2) is

$$B_{1111}>0, \quad B_{1111}+6B_{1122}>0. \tag{12}$$

Since the prototype is centrosymmetrical, Eqs. (6) do not take part. Equations (5) become

$$\begin{aligned} P_x\{B_{11}+2B_{1111}P_x^2+6B_{1122}(P_y^2+P_z^2)\}&=0, \\ P_y\{B_{11}+2B_{1111}P_y^2+6B_{1122}(P_z^2+P_x^2)\}&=0, \\ P_z\{B_{11}+2B_{1111}P_z^2+6B_{1122}(P_x^2+P_y^2)\}&=0. \end{aligned} \tag{13}$$

All the solutions to (13) are, obviously,

(I) $P_x=P_y=P_z=0$;

(II) $P_x^2=-B_{11}/2B_{1111}, \quad P_y=P_z=0$;

(III) $P_x^2=P_y^2=-B_{11}/2(B_{1111}+3B_{1122}), \quad P_z=0$;

(IV) $P_x^2=P_y^2=P_z^2=-B_{11}/2(B_{1111}+6B_{1122})$.

We make a comment. The set

(II′) $P_y^2=-B_{11}/2B_{1111}, \quad P_z=P_x=0$,

and the set

(II″) $P_z^2=-B_{11}/2B_{1111}, \quad P_x=P_y=0$,

for example, are also solutions to (9). These, however, follow naturally from solution II owing to the symmetry of the prototype. Therefore, we need not write them down explicitly.

Solutions I, II, III, and IV correspond, respectively, to the paraelectric phase, the ferroelectric phase of species F*m*3*m*(3)D4, the ferroelectric phase of species F*m*3*m*(6)D2, and the ferroelectric phase of species F*m*3*m*(4)D3. Thus, the ferroelectric phase of species F*m*3*m*(12)A4 is not derived from (11). Therefore, as a conclusion, the describability limit of the species F*m*3*m*(12)A4 must be larger than 4.

2. Species F*m*3*m*(6)D2

The prototypical symmetry of the species F*m*3*m*(6)D2 is the same as that of the species F*m*3*m*(12)A4. Therefore, supposing that the species F*m*3*m*(6)D2 can be described by a free-energy function of fourth degree, this function is given by (11). The solution III to Eqs. (13) corresponds to the species F*m*3*m*(6)D2. We need to examine whether this solution gives a stable phase. Calculating $\Delta\Phi$, we get

$$\Delta\Phi=-B_{11}(\Delta P_x+\Delta P_y)^2-\frac{B_{11}(B_{1111}-3B_{1122})}{B_{1111}+3B_{1122}} \times(\Delta P_x-\Delta P_y)^2+\frac{B_{11}(B_{1111}-3B_{1122})}{B_{1111}+3B_{1122}}(\Delta P_z)^2.$$

(We have chosen the signs of P_x and P_y as positive.) In order that this should always be positive for $\Delta\mathbf{P}\neq0$, the coefficients before $(\Delta P_x+\Delta P_y)^2$, $(\Delta P_x-\Delta P_y)^2$, and $(\Delta P_z)^2$ must all be positive. However, it is impossible that the second and third coefficients should both be positive. Therefore, solution III does not correspond to a stable phase.

Thus, as a conclusion, the describability limit of the species F*m*3*m*(6)D2 must be larger than 4. The orthorhombic phase of barium titanate, $BaTiO_3$, belongs to this species.

3. Species F23(3)D2

We take the coordinate axes parallel to the dyad axes of symmetry of the prototype. It is assumed that the species F23(3)D2 can be described by the free-energy function of fourth degree, which has the form

$$\begin{aligned}\Phi=\Phi_0&+B_{11}(P_x^2+P_y^2+P_z^2)+6B_{123}P_xP_yP_z \\ &+B_{1111}(P_x^4+P_y^4+P_z^4) \\ &+6B_{1122}(P_y^2P_z^2+P_z^2P_x^2+P_x^2P_y^2). \end{aligned}\tag{14}$$

The inequalities (12) must hold. Solving (5) and (6) simultaneously, we obtain, in all, two solutions:

(I) $P_x=P_y=P_z=0$;

(II) $P_x^2=-B_{11}/2B_{1111}, \quad P_y=P_z=0$.

These correspond to the paraelectric phase and the ferroelectric phase of species F23(3)D2, respectively. For the ferroelectric phase, we have

$$\Delta\Phi=-2B_{11}(\Delta P_x)^2+B_{11}(1-3B_{1122}/B_{1111}) \times\{(\Delta P_y)^2+(\Delta P_z)^2\}+6B_{123}P_x\Delta P_y\Delta P_z. \tag{15}$$

A necessary and sufficient condition for (15) to be always positive for $\Delta\mathbf{P}\neq0$ is

$$\begin{gathered} B_{11}<0, \quad 3B_{1122}-B_{1111}>0, \\ 3|B_{123}|<(-2B_{11}/B_{1111})^{1/2}(3B_{1122}-B_{1111}). \end{gathered}\tag{16}$$

There is no inconsistency among these three inequalities.

The condition (10) requires that

$$B_{11}\to0 \quad \text{as} \quad T\to T_c. \tag{17}$$

From this and the third inequality in (16), it follows that

$$B_{123}\to0 \quad \text{as} \quad T\to T_c. \tag{18}$$

According to the postulate of nonmultiple crossing, however, it is impossible that (17) and (18) should be simultaneously satisfied.

Therefore, we conclude that the describability limit of the species F23(3)D2 must be larger than 4. The ferroelectric phase[7] of methylammonium aluminum sulfate dodecahydrate (often abbreviated "MASD"), $(NH_3CH_3)Al(SO_4)_2\cdot12H_2O$, belongs to this species.

4. Species F*mmm*(2)A*m*

We take the coordinate axes perpendicular to the mirror planes of symmetry of the prototype. The free-

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[7] R. Pepinsky, F. Jona, and G. Shirane, Phys. Rev. **102**, 1181 (1956).

energy function of fourth degree has the form

$$\Phi=\Phi_0+B_{11}P_x^2+B_{22}P_y^2+B_{33}P_z^2+B_{1111}P_x^4 +B_{2222}P_y^4+B_{3333}P_z^4+6B_{2233}P_y^2P_z^2 +6B_{3311}P_z^2P_x^2+6B_{1122}P_x^2P_y^2.$$

The species Fmmm(2)Am is separable[1] into three minor species Fmmm(2)Am_a, Fmmm(2)Am_b, and Fmmm(2)Am_c. The argument goes parallel for all these minor species. Let us consider Fmmm(2)Am_c. In this minor species, the spontaneous polarization vector is on the xy plane. Its components satisfy the simultaneous equations

$$B_{11}+2B_{1111}P_x^2+6B_{1122}P_y^2=0,$$
$$B_{22}+6B_{1122}P_x^2+2B_{2222}P_y^2=0, \tag{19}$$

which are reduced forms of the first and second equations in (5), respectively. From (10) and (19), it follows that

$$B_{11}\rightarrow 0,\quad B_{22}\rightarrow 0 \quad \text{as} \quad T\rightarrow T_c. \tag{20}$$

According to the postulate of nonmultiple crossing, however, (20) is impossible. Therefore, as a conclusion, the species Fmmm(2)Am cannot be described by the free-energy function of fourth degree.

5. Species F$\bar{3}m$(3)Dm

We take the z axis parallel to the triad axis of symmetry and the x axis perpendicular to one of the mirror planes of symmetry of the prototype. The free-energy function of fourth degree has the form

$$\Phi=\Phi_0+B_{11}(P_x^2+P_y^2)+B_{33}P_z^2+B_{1111}(P_x^2+P_y^2)^2 +B_{3333}P_z^4+6B_{1133}(P_x^2+P_y^2)P_z^2 +4B_{2223}(P_y^2-3P_x^2)P_yP_z.$$

For the condition (2), it is necessary that

$$B_{1111}>0,\quad B_{3333}>0.$$

In the species F$\bar{3}m$(3)Dm, the spontaneous polarization vector is parallel to the x axis. The P_x is evaluated as

$$P_x^2=-B_{11}/2B_{1111}, \tag{21}$$

from the first equation in (5). The left-hand sides of the second and third equations in (5) vanish automatically when $P_y=P_z=0$. Calculating $\Delta\Phi$, we have

$$\Delta\Phi=-2B_{11}(\Delta P_x)^2+(B_{33}-3B_{11}B_{1133}/B_{1111})(\Delta P_z)^2 +6B_{11}(B_{2223}/B_{1111})\Delta P_y\Delta P_z. \tag{22}$$

It is now evident that (22) is not positive for $\Delta\mathbf{P}$ parallel to the y axis. Therefore, as a conclusion, the species F$\bar{3}m$(3)Dm cannot be described by the free-energy function of fourth degree. This species is one example of the species whose paraelectric phase transitions can be of second order and whose describability limits, nevertheless, must be larger than 4.

6. Species F2/m(1)A2

If the z axis is taken parallel to the dyad axis of symmetry of the prototype, the nonzero coefficients in the free-energy function of fourth degree are

$$B_{11},\ B_{22},\ B_{33},\ B_{12},$$
$$B_{1111},\ B_{2222},\ B_{3333},\ B_{1112},\ B_{2221},$$
$$B_{2233},\ B_{3311},\ B_{1122},\ B_{3312}.$$

In the species F2/m(1)A2, the spontaneous polarization vector is parallel to the xy plane. We take the x axis parallel to the spontaneous polarization vector at each temperature. Then, the first and second equations in (5) become

$$B_{11}+2B_{1111}P_x^2=0,$$
$$B_{12}+2B_{1112}P_x^2=0, \tag{23}$$

respectively. The left-hand side of the third equation in (5) vanishes automatically. In order that the simultaneous equations (23) have a solution, the equality

$$B_{11}/B_{1111}=B_{12}/B_{1112} \tag{24}$$

must hold. In general, the values of B_{ij} and B_{ijkl} depend not only on temperature but also on the choice of the coordinate axes. Equation (24) is just the equation to determine the orientation of the x axis at each temperature. (The orientation of the x axis is determined as the direction such that B_{11}/B_{1111} coincides with B_{12}/B_{1112}.) When (24) holds, (23) have a solution which is the same as (21).

Calculating $\Delta\Phi$, we have

$$\Delta\Phi=-2B_{11}(\Delta P_x)^2-4B_{12}\Delta P_x\Delta P_y +(B_{22}-3B_{11}B_{1122}/B_{1111})(\Delta P_y)^2 +(B_{33}-3B_{11}B_{3311}/B_{1111})(\Delta P_z)^2. \tag{25}$$

A necessary and sufficient condition for (25) to be always positive for $\Delta\mathbf{P}\neq 0$ is

$$B_{11}<0,$$
$$B_{22}-3B_{11}B_{1122}/B_{1111}>0,$$
$$-2B_{12}B_{1112}/B_{1111}<B_{22}-3B_{11}B_{1122}/B_{1111},$$
$$B_{33}-3B_{11}B_{3311}/B_{1111}>0.$$

From (10) and (23), it follows that as T approaches T_c, both B_{11} and B_{12} approach zero. This might appear to be contradictory to the postulate of nonmultiple crossing, but it is not. The reason is that we have chosen the x axis *ad hoc*. (When the postulate of nonmultiple crossing is applied, it is important to know whether there are any other free variables than the temperature.)

After a careful examination, we can see that no inconsistency results from the assumption that the species F2/m(1)A2 is describable by the free-energy function of fourth degree. Hence, we conclude that the describability limit of the species F2/m(1)A2 is 4. The ferroelectric phase[8] of diglycine nitrate, $(NH_2CH_2COOH)_2 \cdot HNO_3$, is one of several real ferroelectrics that are known to belong to this species.

IV. CONCLUSION

We show below the results of the present theory. The following 28 species of ferroelectrics are of describability limit 4:

F$\bar{1}$(1)A1, F2/*m*(1)A2, F2/*m*(1)D2, F222(1)D2, F*mmm*(1)D*m*, F$\bar{4}$(1)D$\bar{4}$, F4/*m*(2)A4, F4/*m*(1)D4, F422(2)D2, F422(1)D4, F$\bar{4}$2*m*(2)D2, F$\bar{4}$2*m*(1)D$\bar{4}$, F4/*mmm*(2)D2, F4/*mmm*(1)D4, F$\bar{3}$(1)D$\bar{3}$, F32(1)D3, F$\bar{3}$*m*(1)D$\bar{3}$, F$\bar{6}$(1)D$\bar{6}$, F6/*m*(1)D6, F622(1)D6, F$\bar{6}$*m*2(1)D$\bar{6}$, F6/*mmm*(1)D6, F*m*3(4)D3, F*m*3(3)D*m*, F432(4)D3, F432(3)D4, F*m*3*m*(4)D3, F*m*3*m*(3)D4.

The describability limits of the other 27 species must be larger than 4.

It is seen that the describability limits of those species whose paraelectric phase transitions are necessarily of first order must all be larger than 4. It is also seen that whereas the species

F$\bar{3}$*m*(3)D*m*, F6/*m*(3)A6, F622(3)D2, F6/*mmm*(3)D2

can[1,3] have paraelectric phase transitions of second order, their describability limits must be larger than 4.

We repeat the following. The describability limit of a ferroelectric is not smaller than the describability limit of the species to which the ferroelectric belongs. The describability limit of a ferroelectric may depend on whether it is under zero stress or under constant strain, but the describability limit of a species does not.

The describability limits of the 27 species, F2/*m*(2)A1 etc., are not all 6; some are larger than 6. Consider, for example, the species F*m*3*m*(24)A1. This is now assumed to be describable by the free-energy function Φ of sixth degree. If we take the coordinate axes parallel to the tetrad axes of symmetry of the prototype, the nonzero coefficients in Φ are

$$B_{11}=B_{22}=B_{33}\,,$$
$$B_{1111}=B_{2222}=B_{3333}\,,\quad B_{2233}=B_{3311}=B_{1122}\,,$$
$$B_{111111}=B_{222222}=B_{333333}\,,\quad B_{112233}\,,$$
$$B_{222233}=B_{333311}=B_{111122}=B_{223333}=B_{331111}=B_{112222}\,.$$

The simultaneous equations (3) become

$$B_{11}+2B_{1111}P_x^2+6B_{1122}(P_y^2+P_z^2)+3B_{111111}P_x^4 +15B_{111122}\{P_y^4+P_z^4+2P_x^2(P_y^2+P_z^2)\} +90B_{112233}P_y^2P_z^2=0\,, \tag{26a}$$

$$B_{11}+2B_{1111}P_y^2+6B_{1122}(P_z^2+P_x^2)+3B_{111111}P_y^4 +15B_{111122}\{P_z^4+P_x^4+2P_y^2(P_z^2+P_x^2)\} +90B_{112233}P_z^2P_x^2=0\,, \tag{26b}$$

$$B_{11}+2B_{1111}P_z^2+6B_{1122}(P_x^2+P_y^2)+3B_{111111}P_z^4 +15B_{111122}\{P_x^4+P_y^4+2P_z^2(P_x^2+P_y^2)\} +90B_{112233}P_x^2P_y^2=0\,; \tag{26c}$$

here, we have taken

$$P_x\neq 0\,,\quad P_y\neq 0\,,\quad P_z\neq 0$$

into account. Subtracting (26c) from (26b), we get

$$(P_y^2-P_z^2)\{2B_{1111}-6B_{1122}+3B_{111111}(P_y^2+P_z^2) +15B_{111122}(2P_x^2-P_y^2-P_z^2)-90B_{112233}P_x^2\}=0\,. \tag{27}$$

Since in general

$$P_y^2\neq P_z^2\,,\quad P_z^2\neq P_x^2\,,\quad P_x^2\neq P_y^2\,, \tag{28}$$

(27) reduces to

$$2B_{1111}-6B_{1122}+3B_{111111}(P_y^2+P_z^2)+15B_{111122} \times(2P_x^2-P_y^2-P_z^2)-90B_{112233}P_x^2=0\,. \tag{29a}$$

In similar fashion, we get

$$2B_{1111}-6B_{1122}+3B_{111111}(P_z^2+P_x^2)+15B_{111122} \times(2P_y^2-P_z^2-P_x^2)-90B_{112233}P_y^2=0\,, \tag{29b}$$

$$2B_{1111}-6B_{1122}+3B_{111111}(P_x^2+P_y^2)+15B_{111122} \times(2P_z^2-P_x^2-P_y^2)-90B_{112233}P_z^2=0\,. \tag{29c}$$

We again subtract (29c) from (29b) and take account of (28). Then we have

$$B_{111111}-15B_{111122}+30B_{112233}=0\,. \tag{30}$$

This equality is to hold over that range of temperature where the ferroelectric phase exists.

It is not, however, considered that an equality like (30) can really hold over a range of temperature (rather than at a special point of temperature)—a postulate.[9] Also, on the other hand, granted that (30) holds, the three equations in (26) lose independence; this means that there does not exist the minimum point of Φ which corresponds to the ferroelectric phase of species F*m*3*m*(24)A1. Therefore, as a conclusion, the describability limit of the species F*m*3*m*(24)A1 must be larger than 6.

We shall take another occasion to determine definitely the describability limit of each of the 27 species—F2/*m*(2)A1, F*m*3*m*(24)A1, etc. In general, the larger describability limits are the more difficult to determine.

We note that the concept of describability limit will play an important role also in our future studies of ferro-ferroelectric phase transitions.

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[8] R. Pepinsky, K. Vedam, S. Hoshino, and Y. Okaya, Phys. Rev. **111**, 430 (1958).

[9] This is the same as the postulate introduced in Ref. 1. It is formally expressed as follows: An expansion coefficient (or, more generally, a combination of expansion coefficients) which is expected, from symmetry considerations, to be nonzero in the prototype does not remain exactly zero over a range of temperature (although it may become exactly zero at one point of temperature).

According to this postulate, two expansion coefficients which are expected, from symmetry considerations, to be unequal in the prototype do not remain exactly equal over a range of temperature (although they may become exactly equal at one point of temperature).