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Possible Species of Ferroelectrics

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A ferroelectric crystal can be considered as a (slight) modification of a certain nonferroelectric ideal crystal which is referred to as the "prototype" of the ferroelectric crystal; in crystallographical symmetry, the prototype should be higher than the ferroelectric crystal and equal to the paraelectric phase if possible. With the aid of the preceding studies and by introducing *a new postulate* on the free energy, which is expected to be generally valid, it is shown theoretically that there are, in all, 55 possible species of ferroelectrics as distinguished according to the point group of the prototype and the total number and orientation of the equivalent unique ferroelectric directions. This theory demands, as a revision of conclusions in previous studies, that 28 (FPT222(2)A2, FPT*mm*2(1)D*m*, and others) of the 83 species of ferro-paraelectric phase transitions must be impossible, and that three (*i*1-I, *i*1-II, and *im*) of the 25 *kinds* of ferroelectrics must be impossible. These theoretical predictions do not conflict with existing observational facts. By the way, the concept of "minor species" is introduced. Some species are able, and sometimes need, to be divided into two or more minor species from a crystallographical point of view. If one minor species is counted as one species, there turn out to be, in all, 67 possible species of ferroelectrics.

1. INTRODUCTION

A CRYSTAL which can become ferroelectric, for a most general case, assumes one paraelectric and several different ferroelectric phases in different regions of temperature. It is possible and convenient for such a crystal to imagine a certain ideal crystal—the "prototype" of that crystal—such that each phase may be considered as a (slight) modification of it. In crystallographical symmetry, the prototype should be higher than any of the ferroelectric phases, and equal to the paraelectric phase. (The concept of prototype holds good even for ferroelectric crystals which have no paraelectric phase transformation.)

Consider, for example, barium titanate, $BaTiO_3$. The well-known four phases—one paraelectric and three ferroelectric—of this crystal can be imagined to be derivatives from a common prototype whose unit cell is cubic and has barium atoms at its apices, oxygen atoms exactly at its face centers, and a titanium atom exactly at its body center.

Previously[1] we made a study of the transition of paraelectric crystals to ferroelectric phases, and found that there are, in all, 83 possible species of ferroelectric phase transitions as distinguished according to the point group of the paraelectric crystal and the total number and orientation of the equivalent unique ferroelectric directions. We assigned[2] new symbols to these 83 species. (In Ref. 2 we used the term "kinds" in place of "species." This must be revised. The term "kinds" is to be used in another sense.)

This result now suggests a new method of classifying the ferroelectrics. That is, to each of the 83 species of *ferro-paraelectric*[3] phase transitions, we can make one species of ferroelectrics correspond. (No ferroelectric should be outside this concept of species.) Thus it turns out that there are, in all, 83 possible species of ferroelectrics as distinguished according to the point group of the *prototype* (rather than the *paraelectric phase*) and the total number and orientation of the equivalent unique ferroelectric directions. It is possible and convenient to represent each of these 83 species of ferroelectrics by almost the same symbol as for the corresponding species of ferro-paraelectric phase transition; we need only to replace "FPT" by "F." The new symbols are as follows:

F$\bar{1}$(1)A1, F*m*(1)D*m*, F2(1)A2, F2/*m*(2)A1,
F2/*m*(1)A2, F2/*m*(1)D2, F222(2)A2, F222(1)D2,
F*mm*2(2)A2, F*mm*2(1)D*m*, F*mmm*(4)A1, F*mmm*(2)A*m*,
F*mmm*(1)D*m*, F4(2)A4, F$\bar{4}$(2)A$\bar{4}$, F$\bar{4}$(1)D$\bar{4}$,
F4/*m*(4)A1, F4/*m*(2)A4, F4/*m*(1)D4, F422(4)A2,
F422(4)A4, F422(2)D2, F422(1)D4, F4*mm*(4)A4,
F4*mm*(2)D*m*, F$\bar{4}$2*m*(4)A2, F$\bar{4}$2*m*(4)A$\bar{4}$, F$\bar{4}$2*m*(2)D*m*,
F$\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}$, F32(3)A2,
F32(1)D3, F3*m*(3)D*m*, F$\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}$, F6(3)A6, F$\bar{6}$(1)D$\bar{6}$,
F6/*m*(6)A1, F6/*m*(3)A6, F6/*m*(1)D6, F622(6)A2,
F622(6)A6, F622(3)D2, F622(1)D6, F6*mm*(6)A6,
F6*mm*(3)D*m*, F$\bar{6}$*m*2(6)A2, F$\bar{6}$*m*2(3)D[$\bar{6}$,2],
F$\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,

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[1] K. Aizu, J. Phys. Soc. Japan **20**, 959 (1965).

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

[3] 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 crystal," "a paraelectric phase transition of a ferroelectric crystal," and "a ferro-paraelectric phase transition" mean the same thing, and differ only in respect to the direction of the investigator's eyes.

F23(6)A2, F23(3)D2, F$m3$(12)A1, F$m3$(6)Am,
F$m3$(4)D3, F$m3$(3)Dm, F432(12)A2, F432(12)A4,
F432(6)D2, F432(4)D3, F432(3)D4,
F$\bar{4}3m$(12)A$\bar{4}$, F$\bar{4}3m$(6)Dm, F$\bar{4}3m$(3)D$\bar{4}$,
F$m3m$(24)A1, F$m3m$(12)A2, F$m3m$(12)A4,
F$m3m$(6)D2, F$m3m$(4)D3, F$m3m$(3)D4.

Each of these symbols consists of four parts. The first part "F" means "ferroelectric." The second part, such as $\bar{1}$, $2/m$, and $m3m$, is the symbol for the point group of the prototype. The third part, such as (1), (4), and (12), shows the number of equivalent unique ferroelectric directions. The last part pertains to the orientation of one of the equivalent unique ferroelectric directions. (For details see Ref. 2.) "Fmmm(2)Am," for example, means the species of ferroelectrics whose prototypes belong to the point group mmm and whose spontaneous polarization vectors are parallel to a mirror plane of symmetry of their prototypes; two equivalent orientations are possible for such a spontaneous polarization vector. "F23(3)D2," as another example, means the species of ferroelectrics whose prototypes belong to the point group 23 and whose spontaneous polarization vectors are parallel to a dyad axis of symmetry of their prototypes; three equivalent orientations are possible for such a spontaneous polarization vector.

Previously[4–7] we also showed that there are, in all, 25 possible kinds of ferroelectrics as distinguished according to their point groups and types of state transition. We represented these 25 kinds by the symbols

$r1$, $i1$-I, $i1$-II, rm, im, $r2$, $i2$-I, $i2$-II,
$rmm2$, $imm2$, $r4$, $i4$, $r4mm$, $r6$, $i6$, $r6mm$,
$r3R$, $i3R$, $r3mR$, $r3P$-I, $r3P$-II,
$i3P$-I, $i3P$-II, $r3mP$-I, $r3mP$-II.

We now thus possess two different classifications for the ferroelectrics—the concept of kinds and the concept of species. The relationship between these two is shown in Ref. 1. Which concept is more convenient depends on the problem being considered. For example, in order to determine the ferroelectric transformations of tensor properties, the concept of kinds is more convenient,[5,6] whereas to determine the orders of ferro-paraelectric phase transitions, the concept of species is more convenient.[2]

We have hitherto been treating all of the 83 species and all of the 25 kinds as possible in general theories of ours, not because we have positively verified their possibility, but only because we have not been able to find any reason for their impossibility.

For general theories, it may be natural that species or kinds which cannot be found to be impossible at one stage of development in the theories should all be treated as possible at that stage. As the theories progress, however, it might happen that at a higher stage of development some of those species or kinds would turn out to be impossible. Then these should be excluded from the general theories.

In the following sections, we introduce a new postulate on the free energy of the crystal which we consider to be very reasonable. This postulate gives rise to a new criterion for the possibility of species. We apply this criterion to all of the 83 species to test their possibility. This test for species becomes also a test for kinds.

As a result, we shall find that 28 of the 83 species and 3 of the 25 kinds should be impossible. These theoretical predictions do not conflict with existing observational facts. If in future, however, a ferroelectric should be discovered which belongs to one of the 28 species or to one of the three kinds, then our present postulate would be concluded not to be generally valid.

2. ILLUSTRATION OF THE THEORY

A. Case of Point Group 222

We examine, in this section, not all of the 83 species of ferroelectrics but only several representatives. The arguments about the other species are similar and so will be omitted. We first consider the species of ferroelectrics whose prototypes belong to the point group 222. These species are F222(2)A2 and F222(1)D2. We assume, for the present, that the free energy (under zero stress) Φ can be expressed as a finite power series in the components P_x, P_y, P_z of the polarization vector:

$$\Phi=\Phi_0+\sum_{ij} B_{ij}P_iP_j+\sum_{ijk} B_{ijk}P_iP_jP_k +\sum_{ijkl} B_{ijkl}P_iP_jP_kP_l+\sum_{ijklm} B_{ijklm}P_iP_jP_kP_lP_m +\sum_{ijklmn} B_{ijklmn}P_iP_jP_kP_lP_mP_n,$$

where Φ_0, B_{ij}, B_{ijk}, $\cdots$, B_{ijklmn} depend on temperature alone. (It will later be seen that this assumption is not essential.) We take the rectangular coordinate axes x, y, z parallel to the dyad axes of symmetry of the prototype. Then, from symmetry consideration, the nonzero coefficients are

$$B_{11},\ B_{22},\ B_{33};\quad B_{123};$$
$$B_{1111},\ B_{2222},\ B_{3333},\ B_{2233},\ B_{3311},\ B_{1122};$$
$$B_{11123},\ B_{22231},\ B_{33312};$$
$$B_{111111},\ B_{222222},\ B_{333333},\ B_{111122},\ B_{111133};$$
$$B_{222233},\ B_{222211},\ B_{333311},\ B_{333322},\ B_{112233}.$$

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[4] K. Aizu, Rev. Mod. Phys. 34, 550 (1962).
[5] K. Aizu, Phys. Rev. 133, A1350 (1964).
[6] K. Aizu, Phys. Rev. 134, A701 (1964).
[7] K. Aizu, J. Phys. Soc. Japan 20, 284 (1965).

The components of the spontaneous polarization vector must satisfy the simultaneous equations

$$\partial\Phi/\partial P_x=0,\quad \partial\Phi/\partial P_y=0,\quad \partial\Phi/\partial P_z=0. \qquad (1)$$

They must furthermore satisfy the simultaneous equations which result from replacing P_x, P_y, P_z in the left-hand sides of (1) by $-P_x$, $-P_y$, $-P_z$; for, the two senses opposite to each other of the spontaneous polarization vector should be completely equivalent. This latter condition, however, need not be cared about, because the 83 species are all such that if the former condition is satisfied, the latter condition is automatically satisfied.

Calculating the left-hand sides of (1), we have

$$\begin{aligned}\partial\Phi/\partial P_x=\ & 2B_{11}P_x+6B_{123}P_yP_z+4B_{1111}P_x^3\\ &+12B_{1122}P_y^2P_x+12B_{3311}P_z^2P_x\\ &+20B_{22231}P_y^3P_z+20B_{33312}P_z^3P_y\\ &+60B_{11123}P_x^2P_yP_z+6B_{111111}P_x^5\\ &+30B_{222211}P_y^4P_x+30B_{333311}P_z^4P_x\\ &+60B_{111122}P_x^3P_y^2+60B_{111133}P_x^3P_z^2\\ &\qquad\qquad+180B_{112233}P_y^2P_z^2P_x,\\ \partial\Phi/\partial P_y=\ & 2B_{22}P_y+6B_{123}P_zP_x+4B_{2222}P_y^3\\ &+12B_{2233}P_z^2P_y+12B_{1122}P_x^2P_y\\ &+20B_{33312}P_z^3P_x+20B_{11123}P_x^3P_z\\ &+60B_{22231}P_y^2P_zP_x+6B_{222222}P_y^5\\ &+30B_{333322}P_z^4P_y+30B_{111122}P_x^4P_y\\ &+60B_{222233}P_y^3P_z^2+60B_{222211}P_y^3P_x^2\\ &\qquad\qquad+180B_{112233}P_z^2P_x^2P_y,\\ \partial\Phi/\partial P_z=\ & 2B_{33}P_z+6B_{123}P_xP_y+4B_{3333}P_z^3\\ &+12B_{3311}P_x^2P_z+12B_{2233}P_y^2P_z\\ &+20B_{11123}P_x^3P_y+20B_{22231}P_y^3P_x\\ &+60B_{33312}P_z^2P_xP_y+6B_{333333}P_z^5\\ &+30B_{111133}P_x^4P_z+30B_{222233}P_y^4P_z\\ &+60B_{333311}P_z^3P_x^2+60B_{333322}P_z^3P_y^2\\ &\qquad\qquad+180B_{112233}P_x^2P_y^2P_z.\end{aligned}$$

We examine species F222(2)A2. In this species, since the spontaneous polarization vector is perpendicular to one—say the z axis—of the dyad axes of symmetry, Eqs. (1) become

$$\begin{aligned}&B_{11}+2B_{1111}P_x^2+6B_{1122}P_y^2+3B_{111111}P_x^4\\ &\qquad+30B_{111122}P_x^2P_y^2+15B_{222211}P_y^4=0,\\ &B_{22}+6B_{1122}P_x^2+2B_{2222}P_y^2+15B_{111122}P_x^4 \qquad (2)\\ &\qquad+30B_{222211}P_x^2P_y^2+3B_{222222}P_y^4=0,\\ &3B_{123}+10B_{11123}P_x^2+10B_{22231}P_y^2=0.\end{aligned}$$

Viewing (2), we notice that there are too many equations for the number of unknown quantities. It is, therefore, evident that for P_x and P_y to be able to satisfy these three equations simultaneously, one special relation must hold among the coefficients B in the range of temperature where the relevant ferroelectric phase appears. We cannot, however, find any natural reason why such a special relation must hold. Here, therefore, we explicitly postulate that such a special relation does not hold.[8] According to this postulate, there should be no solution to the simultaneous Eqs. (2). This leads to the conclusion that the species F222(2)A2 should be impossible.

In the above argument, we have assumed that Φ can be expressed as a finite power series in P_x, P_y, P_z. This assumption is, however, dispensable, as will become evident below. For brevity let us use the letters "x, y, z" instead of "P_x, P_y, P_z." In order to show that Φ is a function of x, y, z, let us write "$\Phi(x,y,z)$." Since the prototype belongs to the point group 222, the identities

$$\Phi(x,y,z)=\Phi(x,-y,-z)=\Phi(-x,y,-z) \qquad (3)$$

hold. These are all independent relations of symmetry that $\Phi(x,y,z)$ must satisfy. Differentiating (3) with respect to x, y, z, we get the identities

$$\begin{aligned}\Phi_x(x,y,z)&=\Phi_x(x,-y,-z)=-\Phi_x(-x,y,-z),\\ \Phi_y(x,y,z)&=-\Phi_y(x,-y,-z)=\Phi_y(-x,y,-z), \qquad (4)\\ \Phi_z(x,y,z)&=-\Phi_z(x,-y,-z)=-\Phi_z(-x,y,-z).\end{aligned}$$

In species F222(2)A2, the x and y components of the spontaneous polarization vector must satisfy the simultaneous equations

$$\Phi_x(x,y,0)=0,\quad \Phi_y(x,y,0)=0,\quad \Phi_z(x,y,0)=0. \qquad (5)$$

It is noticed that there are too many equations for the number of unknown quantities.

In general, when there are too many equations for the number of unknown quantities, we must discern whether there are *essentially* or only *apparently* too many equations. The latter case occurs when one or two of the equations should hold for any values of the unknown quantities, as is required from symmetry.

For F222(2)A2, we cannot find any natural cause for the number of equations becoming two in essence. The relations (4) only serve to inform us that if the set (x,y) is a solution to the simultaneous Eqs. (5), the sets $(x,-y)$ and $(-x,y)$ are also solutions to (5). For F222(2)A2, thus, it is considered that, in (5), the number of equations is essentially larger than the number of unknown quantities.

Here, we postulate generally that in a set of simultaneous equations like (5), when the number of equations is essentially larger than the number of unknown quantities, there exists no solution which continues in a range of temperature. (The solution must not be such that some of the unknown quantities are identically zero. For, if the solution is such, it should correspond to another species.)

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[8] Although no natural reason can be discovered why such a special relation must hold, on the other hand, neither can a decisive reason be found why such a special relation must *not* hold in any case. It is just for this sake that we "postulate."

According to this postulate, (5) should have no appropriate solution for F222(2)A2. It is therefore considered that F222(2)A2 is impossible.

In species F222(1)D2, since the spontaneous polarization vector is parallel to one—say the z axis—of the dyad axes of symmetry, its z component must satisfy the simultaneous equations

$$\Phi_x(0,0,z)=0, \quad \Phi_y(0,0,z)=0, \quad \Phi_z(0,0,z)=0. \tag{6}$$

In (6), while the number of unknown quantities is one, the number of equations is three. This inequality is, however, only apparent, because it is evident from (4) that the first and second equalities in (6) hold for any value of z. Therefore, (6) may have a (nonzero) solution. F222(1)D2 cannot thus be concluded to be impossible; it should be treated as possible.

B. Cases of Point Groups m, 2, and $2/m$

For a second example, we consider the species whose prototype belongs to the point group m. This species is Fm(1)Dm. We take the z axis perpendicular to the mirror plane of symmetry of the prototype. The identity

$$\Phi(x,y,z)=\Phi(x,y,-z) \tag{7}$$

holds. This is the only relation of symmetry that $\Phi(x,y,z)$ must satisfy. Differentiating (7) with respect to x, y, z, we get the identities

$$\begin{aligned}\Phi_x(x,y,z)&=\Phi_x(x,y,-z),\\ \Phi_y(x,y,z)&=\Phi_y(x,y,-z),\\ \Phi_z(x,y,z)&=-\Phi_z(x,y,-z).\end{aligned} \tag{8}$$

The z component of the spontaneous polarization vector must satisfy the simultaneous Eqs. (6). The relations (8) only tell us that if z is a solution to (6), $-z$ is also a solution to (6). It is evident that in (6), while there is one unknown quantity, there are essentially three equations. Hence, according to the postulate, Fm(1)Dm must be impossible.

This result is very important to us. We have hitherto been treating the kind i1-I as possible; this may be natural so long as its impossibility cannot be verified. Now, however, we find i1-I to be impossible, as follows. The *primitive* phase transition of the ferroelectrics of kind i1-I is nothing but FPTm(1)Dm.[1,2] FPTm(1)Dm is, however, impossible because Fm(1)Dm is impossible. Hence the primitive phase transition for the kind i1-I is impossible. This means that the kind i1-I is impossible.

For a third example, we consider the species whose prototype belongs to the point group 2. This species is F2(1)A2. We take the z axis parallel to the dyad axis of symmetry. The relation of symmetry of $\Phi(x,y,z)$ is

$$\Phi(x,y,z)=\Phi(-x,-y,z). \tag{9}$$

Therefore, we have the identities

$$\begin{aligned}\Phi_x(x,y,z)&=-\Phi_x(-x,-y,z),\\ \Phi_y(x,y,z)&=-\Phi_y(-x,-y,z),\\ \Phi_z(x,y,z)&=\Phi_z(-x,-y,z).\end{aligned} \tag{10}$$

The x and y components of the spontaneous polarization vector must satisfy the simultaneous Eqs. (5). The relations (10) only tell us that if the set (x,y) is a solution to (5), the set $(-x,-y)$ is also a solution to (5). It is evident that in (5), the number of equations is essentially larger than the number of unknown quantities. Hence, according to the postulate, F2(1)A2 must be impossible. This result is also very important to us. It leads to the conclusion that the kind i1-II must be impossible, because the primitive phase transition of the ferroelectrics of this kind is just FPT2(1)A2.[1,2]

We examine the species whose prototype belongs to the point group $2/m$. These species are F$2/m$(2)A1, F$2/m$(1)A2, and F$2/m$(1)D2. We take the z axis parallel to the dyad axis of symmetry. The identities

$$\Phi(x,y,z)=\Phi(x,y,-z)=\Phi(-x,-y,z) \tag{11}$$

hold. Therefore, we have the identities

$$\begin{aligned}\Phi_x(x,y,z)&=\Phi_x(x,y,-z)=-\Phi_x(-x,-y,z),\\ \Phi_y(x,y,z)&=\Phi_y(x,y,-z)=-\Phi_y(-x,-y,z),\\ \Phi_z(x,y,z)&=-\Phi_z(x,y,-z)=\Phi_z(-x,-y,z).\end{aligned} \tag{12}$$

In F$2/m$(1)D2, the z component of the spontaneous polarization vector must satisfy the simultaneous Eqs. (6). It is evident from (12) that the first and second equalities in (6) hold for any value of z. Hence the number of equations in (6) is, in essence, one. Therefore we cannot conclude that F$2/m$(1)D2 is impossible; we should treat this species as possible. Incidentally, it is seen that the kind r2 is also not shown to be impossible; the primitive phase transition of the ferroelectrics of this kind belongs to FPT$2/m$(1)D2.[1,2]

In F$2/m$(1)A2, the x and y components of the spontaneous polarization vector must satisfy the simultaneous Eqs. (5). It is evident from (12) that the third equality in (5) holds for any values of x and y. Hence the number of equations in (5) is, in essence, two. Therefore, F$2/m$(1)A2 is not shown to be impossible. Incidentally, the kind rm is also not shown to be impossible; the primitive phase transition of the ferroelectrics of this kind belongs to FPT$2/m$(1)A2.[1,2]

In F$2/m$(2)A1, the x, y, and z components of the spontaneous polarization vector must satisfy the simultaneous equations

$$\Phi_x(x,y,z)=0, \quad \Phi_y(x,y,z)=0, \quad \Phi_z(x,y,z)=0. \tag{13}$$

The number of equations is equal to the number of unknown quantities. Therefore, F$2/m$(2)A1 is not shown to be impossible.

C. Case of Point Group *mm*2

The species whose prototype belongs to the point group *mm*2 are F*mm*2(2)A2 and F*mm*2(1)D*m*. We take the z axis parallel to the dyad axis of symmetry, and the x axis perpendicular to one of the mirror planes of symmetry. It holds that

$$\Phi(x,y,z)=\Phi(-x,\,y,\,z)=\Phi(x,\,-y,\,z)\,, \qquad (14)$$

and hence that

$$\begin{aligned}\Phi_x(x,y,z)&=-\Phi_x(-x,\,y,\,z)=\Phi_x(x,\,-y,\,z)\,,\\ \Phi_y(x,y,z)&=\Phi_y(-x,\,y,\,z)=-\Phi_y(x,\,-y,\,z)\,, \qquad (15)\\ \Phi_z(x,y,z)&=\Phi_z(-x,\,y,\,z)=\Phi_z(x,\,-y,\,z)\,.\end{aligned}$$

In F*mn*2(1)D*m*, the x component of the spontaneous polarization vector must satisfy the simultaneous equations

$$\Phi_x(x,0,0)=0\,,\quad \Phi_y(x,0,0)=0\,,\quad \Phi_z(x,0,0)=0\,. \qquad (16)$$

From the relations (15), it follows that the second equality in (16) should hold for any value of x, but not that the first or third equality should hold for any value of x. Hence the number of equations is, in essence, two. Therefore, F*mm*2(1)D*m* must be impossible. From this result we also see that the kind *im* should be impossible, since the primitive phase transition of the ferroelectrics of this kind belongs to FPT*mm*2(1)D*m*.[1,2]

In F*mm*2(2)A2, the x and y components of the spontaneous polarization vector must satisfy the simultaneous Eqs. (5). The number of equations is not diminished by the relations (15), and hence is essentially three. Therefore, F*mm*2(2)A2 must be impossible. This result is also evident from the fact[1] that F*mm*2(2)A2 should belong to the kind *i*1-II which has been found to be impossible.

D. Case of Point Group $\bar{3}$

The species whose prototype belongs to the point group $\bar{3}$ are F$\bar{3}$(3)A1 and F$\bar{3}$(1)D$\bar{3}$. We take the z axis parallel to the inversion triad axis of symmetry. It may be seen that

$$\Phi(x,y,z)=\Phi(\tfrac{1}{2}x-\tfrac{1}{2}\sqrt{3}y,\,\tfrac{1}{2}\sqrt{3}x+\tfrac{1}{2}y,\,-z)\,, \qquad (17)$$

and hence that

$$\begin{aligned}\Phi_x(x,y,z)&=\tfrac{1}{2}\Phi_x(\tfrac{1}{2}x-\tfrac{1}{2}\sqrt{3}y,\,\tfrac{1}{2}\sqrt{3}x+\tfrac{1}{2}y,\,-z)\\ &\quad+\tfrac{1}{2}\sqrt{3}\Phi_y(\tfrac{1}{2}x-\tfrac{1}{2}\sqrt{3}y,\,\tfrac{1}{2}\sqrt{3}x+\tfrac{1}{2}y,\,-z)\,,\\ \Phi_y(x,y,z)&=-\tfrac{1}{2}\sqrt{3}\Phi_x(\tfrac{1}{2}x-\tfrac{1}{2}\sqrt{3}y,\,\tfrac{1}{2}\sqrt{3}x+\tfrac{1}{2}y,\,-z)\\ &\quad+\tfrac{1}{2}\Phi_y(\tfrac{1}{2}x-\tfrac{1}{2}\sqrt{3}y,\,\tfrac{1}{2}\sqrt{3}x+\tfrac{1}{2}y,\,-z)\,, \qquad (18)\\ \Phi_z(x,y,z)&=-\Phi_z(\tfrac{1}{2}x-\tfrac{1}{2}\sqrt{3}y,\,\tfrac{1}{2}\sqrt{3}x+\tfrac{1}{2}y,\,-z)\,.\end{aligned}$$

In F$\bar{3}$(1)D$\bar{3}$, the z component of the spontaneous polarization vector must satisfy the simultaneous equations (6). Since, from the relations (18),

$$\begin{aligned}\Phi_x(0,0,z)&=\tfrac{1}{2}\Phi_x(0,\,0,\,-z)+\tfrac{1}{2}\sqrt{3}\Phi_y(0,\,0,\,-z)\,,\\ \Phi_y(0,0,z)&=-\tfrac{1}{2}\sqrt{3}\Phi_x(0,\,0,\,-z)+\tfrac{1}{2}\Phi_y(0,\,0,\,-z)\,,\\ \Phi_x(0,\,0,\,-z)&=\tfrac{1}{2}\Phi_x(0,0,z)+\tfrac{1}{2}\sqrt{3}\Phi_y(0,0,z)\,,\\ \Phi_y(0,\,0,\,-z)&=-\tfrac{1}{2}\sqrt{3}\Phi_x(0,0,z)+\tfrac{1}{2}\Phi_y(0,0,z)\,,\end{aligned}$$

it is evident that the first and second equalities in (6) hold for any value of z. Therefore, F$\bar{3}$(1)D$\bar{3}$ is not shown to be impossible. Incidentally, the kinds *r*3*R* and *r*3*P*-I are also not shown to be impossible; the primitive phase transition of the ferroelectrics of kind *r*3*R* or *r*3*P*-I belongs to FPT$\bar{3}$(1)D$\bar{3}$.[1,2]

In F$\bar{3}$(3)A1, the components of the spontaneous polarization vector must satisfy the simultaneous Eqs. (13). The number of equations is equal to the number of unknown quantities. Therefore, F$\bar{3}$(3)A1 is not shown to be impossible.

3. CONCLUSION

Those of the 83 species of ferroelectrics which have not appeared in Sec. 2 can be examined in a similar manner. We omit the arguments about them. As a final result, it is found that only 55 of the 83 species survive under the application of the present criterion. These 55 species should all be treated as possible, as long as they cannot be proved to be impossible. We show the symbols for the 55 possible species in Table I.

It is noted from the table that no prototypes of ferroelectrics belong to a polar point group,[9] and that a ferroelectric derived from a noncentrosymmetric prototype is necessarily of "D type," i.e., such that the orientation of the spontaneous polarization vector is crystallographically *definite*.

It is possible, and sometimes necessary, for some species to be clearly divided into two or more "minor species" from a crystallographical point of view. In the species F*mmm*(2)A*m*, for example, the three mirror planes of symmetry are not equivalent to one another. Therefore this species can be divided into three minor species according to which of these mirror planes of symmetry the spontaneous polarization vector is parallel to. If necessary, we shall represent these minor species by the symbols

F*mmm*(2)Am_a, F*mmm*(2)Am_b, F*mmm*(2)Am_c,

or the symbols

F*mmm*(2)Am_1, F*mmm*(2)Am_2, F*mmm*(2)Am_3.

(The subscripts "*a*, *b*, *c*" mean the crystallographic principal axes.) In the species F422(2)D2, as another example, the four dyad axes of symmetry are not all

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[9] This should not be considered as a foregone conclusion. It is to be disputed whether or not a spontaneous polarization can emerge (at a transition temperature) in a direction perpendicular to the unique polar axis of a paraelectric crystal which belongs to a polar point group.

TABLE I. The 55 possible species of ferroelectrics and the number of minor species for each of them.

System of the prototype	Species	Number of minor species
Triclinic	F$\bar{1}$(1)A1	...
Monoclinic	F2/*m*(2)A1	...
	F2/*m*(1)A2	...
	F2/*m*(1)D2	...
Orthorhombic	F222(1)D2	3
	F*mmm*(4)A1	...
	F*mmm*(2)A*m*	3
	F*mmm*(1)D*m*	3
Tetragonal	F$\bar{4}$(1)D$\bar{4}$	...
	F4/*m*(4)A1	...
	F4/*m*(2)A4	...
	F4/*m*(1)D4	...
	F422(2)D2	2
	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	2
	F4/*mmm*(4)A4	...
	F4/*mmm*(2)D2	2
	F4/*mmm*(1)D4	...
Trigonal	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$\bar{3}$	...
Hexagonal	F$\bar{6}$(1)D$\bar{6}$	...
	F6/*m*(6)A1	...
	F6/*m*(3)A6	...
	F6/*m*(1)D6	...
	F622(3)D2	2
	F622(1)D6	...
	F$\bar{6}$*m*2(1)D$\bar{6}$	...
	F6/*mmm*(12)A1	...
	F6/*mmm*(6)A2	2
	F6/*mmm*(6)A6	...
	F6/*mmm*(3)D2	2
	F6/*mmm*(1)D6	...
Cubic	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	...

equivalent, but only each two that are perpendicular are equivalent. Therefore this species can be divided into two minor species according to which dyad axis of symmetry the spontaneous polarization vector is parallel to. If necessary, we shall represent these minor species by the symbols

F422(2)D2_a, F422(2)D2_d,

or the symbols

F422(2)D2_1, F422(2)D2_2.

(The subscript "*d*" means "diagonal.") In Table I we show the number of minor species for the species distinguishable into two or more minor species. It is noted that if one minor species is counted as one species, there are, in all, 67 possible species of ferroelectrics.

A test of the possibility of species becomes also a test of the possibility of kinds. The present test indicates that the three kinds,

i1-I, *i1*-II, *im*,

are impossible. (See Sec. 2.) The other 22 kinds,

r1, *rm*, *r2*, *i2*-I, *i2*-II, *rmm2*, *imm2*,
r4, *i4*, *r4mm*, *r6*, *i6*, *r6mm*,
r3R, *i3R*, *r3mR*, *r3P*-I, *r3P*-II,
i3P-I, *i3P*-II, *r3mP*-I, *r3mP*-II,

have not been found to be impossible; these should be treated as possible.

Previously[2] we determined theoretically the orders of the ferro-paraelectric phase transitions, and found that 50 of the 83 species of ferro-paraelectric phase transitions must be of first order, and that the other 33 species can be either of first order or of second order. Now, however, we know that the 83 species are not all possible,[10] and hence we must restate the conclusion as follows: 23 of the 55 species of ferro-paraelectric phase transitions must be of first order, and the other 32 species can be either of first order or of second order. If represented not by the symbols for *ferro-paraelectric phase transitions* but by the symbols for *ferroelectrics*, the 23 species are

F2/*m*(2)A1, F*mmm*(4)A1, F*mmm*(2)A*m*, F4/*m*(4)A1,
F4/*mmm*(8)A1, F4/*mmm*(4)A2, F4/*mmm*(4)A4,
F$\bar{3}$(3)A1, F$\bar{3}$*m*(6)A1, F$\bar{3}$*m*(3)A*m*, F6/*m*(6)A1,
F6/*mmm*(12)A1, F6/*mmm*(6)A2, F6/*mmm*(6)A6,
F23(3)D2, F*m*3(12)A1, F*m*3(6)A*m*, F432(6)D2,
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.

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[10] If a species of ferroelectrics is impossible, the corresponding species of ferro-paraelectric phase transitions is also impossible. Therefore, only 55 of the 83 species of ferro-paraelectric phase transitions are, henceforth, to be treated as possible.

It is convenient to refer to a ferroelectric as being *primitive* or *complex* according to whether the number of equivalent unique ferroelectric directions of its species is 1 or larger. We note as a "theorem" that the paraelectric phase transition of every primitive ferroelectric can be of either first or second order. (We shall in the future discuss the relationship between the concepts of primitiveness and complexity for *ferroelectrics* and those for *ferro-paraelectric phase transitions*.)

A crystal which can become ferroelectric, in the most general case, assumes several different ferroelectric phases in different regions of temperature. It is presumed that in most cases—but not all—the prototypes of such ferroelectric phases are one and the same. (It may also be possible that one crystal has two or more different prototypes in different regions of temperature.) In future when a systematic investigation is made into ferro-ferroelectric phase transitions, the concepts of prototypes and species (and minor species) will play an important role.

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Relativistic Energy Bands for Thorium, Actinium, and Lutetium*

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The electronic energy bands have been calculated for Lu, Th, and Ac using the relativistic augmented-plane-wave method. The importance of the relativistic effects in the rare earths is typified by the results for Lu which show that the details of the Fermi surface will be altered considerably by these effects. As indicated by the bands for Th and Ac, the relativistic effects will be even more striking for the actinide series.

WE have calculated the electronic energy bands in Lu, Th, and Ac, with particular reference to relativistic effects. There is currently considerable interest in the electronic structures of both the lanthanides and the actinides, and it is apparent from our results that it is essential to consider such relativistic effects in the interpretation of any experimental results. We have studied Lu because it is the heaviest of the lanthanides and has approximately the same electronic structure as Gd, Tb, Dy, Ho, Er, and Tm. Hence, the discussion for Lu should be applicable to all of the heavier $4f$ rare earths, with the exception of Yb which has a different crystal structure. Th and Ac were studied because they are not complicated by the presence of a slightly filled $5f$ band which would require very careful consideration of the self-consistency of the crystal potential. Thus, attention can be concentrated on the rather striking relativistic effects manifested in these heavy elements.

The energy bands were computed using the relativistic augmented-plane-wave (APW) method[1] which has already been successfully applied to tungsten[2] and lead.[3] The potential was constructed from the relativistic atomic self-consistent-field calculations of Liberman, Waber and Cromer.[4] The importance of treating the atomic calculation relativistically has been discussed by these authors and by others.[5] Exchange was treated in the Slater $\rho^{1/3}$ approximation,[6] both in the atomic calculations and in the construction of the muffin-tin

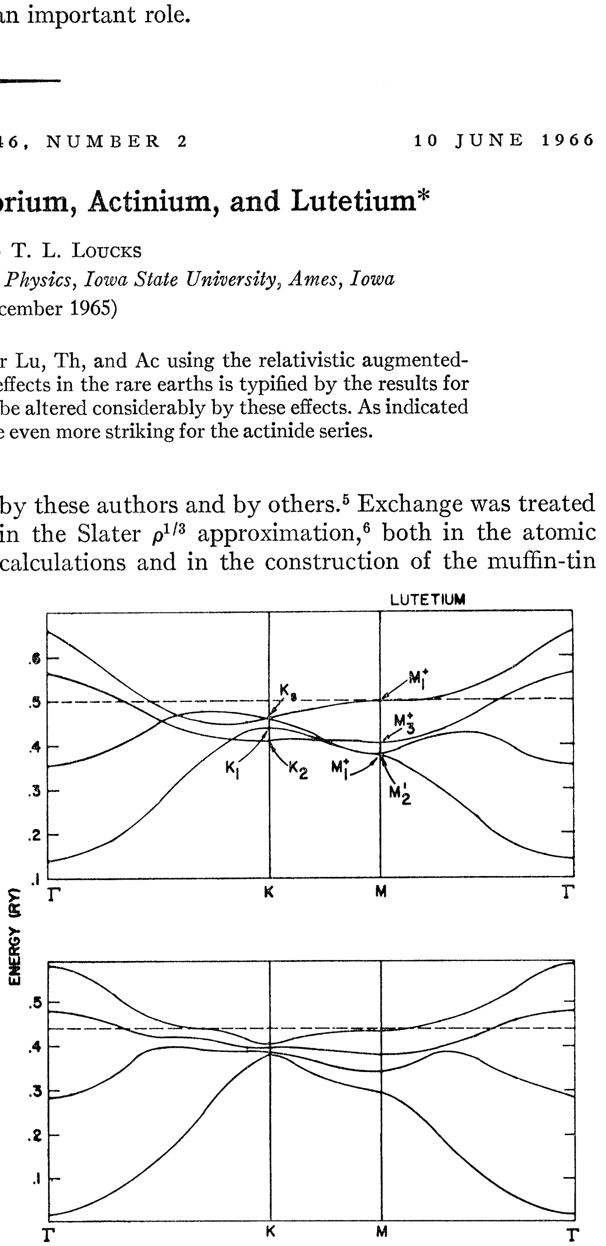

FIG. 1. Nonrelativistic (upper) and relativistic (lower) energy bands for lutetium. The dashed lines give the approximate Fermi energy.

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